

**STUDY ON SYNTHESIS OF LIMESTONE CALCINED
CLAY CEMENT (LC3) CONCRETE USING LOCAL
CLAYS AND ITS DURABILITY**

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CIVIL AND ENVIRONMENTAL ENGINEERING

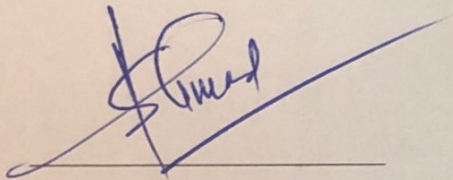
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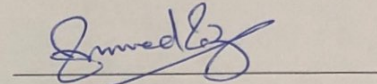
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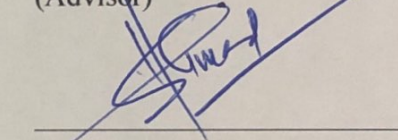
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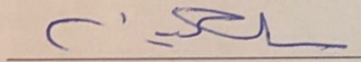
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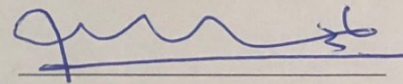
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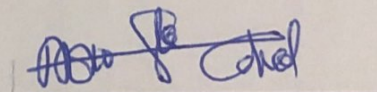
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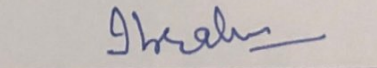
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| I dedicate this work to my parents and family |

ACKNOWLEDGMENTS

First of all, I would like to thank God for giving me the guidance in my life and giving me the power and patient to accomplish my dreams of reaching to this point where I am standing now.

Secondly, I would like to thank my parents who raised me to be who I am now, for being patient with me through all my life and for the love they gave me in my life.

I also would like to thank KFUPM for giving me the opportunity to study and get master degree under their name. I would like to thank my advisor Dr. Hammad Raza Khalid for helping me through my studying and accomplishing this thesis. I would like to thank Dr. Mohammed Al-Osta for giving me advices through my studying in KFUPM and encouraging me to give the best I can. I also would like to thank my committee members Dr. Mohammed Al-Osta, Prof. Shamsad Ahmad, Dr. Muhammad Ibrahim and Dr. Saheed Adekunle for being patient and giving my help in my work whenever I needed.

I would also like to thank all the lab engineers at Civil Engineering Department that helped and teach me how to use the lab equipment needed in my work and allowing me to use the lab as needed in my thesis duration.

I would like to give special thanks to my colleague Ibrahim Nabil Al-Duais who gives me a lot of help in the whole time of my work.

Finally, I would like to give my greatest gratitude to my family for helping me through life to reach to this point and my entire friends that encouraging me to accomplish my academic goals.

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ABSTRACT

Full Name : [Marwan Abdulrazzaq Abdullah Abdulqader]
Thesis Title : [Study on synthesis of limestone calcined clay cement (LC3) concrete using local clays and its durability]
Major Field : [Civil and Environmental Engineering]
Date of Degree : [May 2022]

It is well known in construction industry that Portland cement (clinker) production emitting high amount of CO₂ to the atmosphere. Clinker reduction in concrete is an active research area. Different supplementary cementations materials, SCMs (mainly coal fly ash and blast furnace slag) can be used to partially replace clinker in concrete. However, most of these SCMs are available in limited quantity. Limestone calcined clay cement (LC3) cement is one of the new types of concrete which has grabbed the attention of many researchers. This new cement is made by reducing the amount of clinker by replacing it with calcined kaolinite clays (metakaolin) by around 30% and limestone by about 15% or more. This reduction of clinker will provide a concrete that produce less amount of CO₂. This will lead to new green concrete while at the same time it keeps the physical and mechanical properties of the concrete with minor changes in comparison with ordinary Portland cement in both fresh and hardened concrete.

In this study, investigation of the locally available clays and check their suitability for LC3 concrete. In order to do that first, characterization of the local clays using X-ray diffraction (XRD) and thermo gravimetric analysis (TGA) to find the phases and kaolinite content. The promising clays will be used to make LC3 concrete. The fresh (e.g., slump, setting time) and hardened concrete properties (mechanical strength) will be determined by

relevant tests. Then the durability aspect of prepared LC3 concrete (i.e., acid attack, chloride permeability, and sulfate resistance) will be evaluated in detail.

ملخص الرسالة

الاسم الكامل: مروان عبدالرزاق عبدالله القادر

عنوان الرسالة: دراسة تركيب الاسمنت الطيني بالحجر الجيري المعالج بالحرارة (LC3) باستخدام الطين المحلي ومقاومته.

التخصص: الهندسة المدنية والبيئية

تاريخ الدرجة العلمية: مايو 2022

مجال الصناعة الانشائية يعرف بأنه صناعة الأسمنت من أكثر المجالات المسببة لانبعاث غاز ثاني اكسيد الكربون في الغلاف الجوي. أحد مجالات البحث النشطة تعمل على تقليل استخدام الاسمنت في الخرسانات من اجل تقليل اضرارها. إنه بالإمكان استخدام مواد اسمنتية تكمله من اجل التقليل جزئيا من كمية الاسمنت المستخدم مثل رماد الفحم ومخلفات افران الصهر ولكن كمية توفر هذه المواد محدودة مقارنة بالإنتاج المطلوب للمواد الاسمنتية. خلطة الاسمنت الطيني بالحجر الجيري المعالج بالحرارة هو أحد الأنواع الجديدة التي جذبت انتهاء العديد من الباحثين لاستخدامها كمادة لتقليل استخدام الاسمنت. هذه الخلطة الجديدة تعمل على تقليل استخدام الاسمنت بإحلاله بالطين المعالج بالحرارة المحتوي على مادة الميكاكولين بنسبة 30% وباستخدام الحجر الجيري بنسبة 15% او أكثر. باستخدام هذه الخلطة من الممكن تقليل كمية الاسمنت المستخدمة في الخرسانات وبالتالي تقليل انبعاثات غاز ثاني اكسيد الكربون. تعد هذه الخلطة أحد انواع الخرسانات الصديقة للبيئة بالتزامن مع حفاظها على خصائص الخرسانة العادية الميكانيكية والفيزيائية مع بعض الاختلافات البسيطة في خصائصها الأولية.

هذه الدراسة تركز على دراسة الطين المحلي المتوفر وامكانية استخدامه في خلطة الاسمنت الطيني بالحجر الجيري المعالج بالحرارة وذلك بالتحقق منه باستخدام الاختبارات التحليل باستخدام اختبارات الأشعة السينية واختبارات القياس الحراري للتحقق من كفاءة الطين المحلي وتوفر مادة الكاولين فيه. الاختبارات الأولية (لدونة الخرسانة) والاختبارات الصلبة للخرسانة (صلابة وقوة الخرسانة) سيتم اختبارها للخلطة الجديدة وايضا اختبارات تحمل الخرسانة للعوامل البيئية مثل التعرض للأسيد والكبريتات وايضا اختراق الاملاح للخرسانة سيتم دراستها بالتفصيل.

INTRODUCTION

During the last few decades, there is an increased awareness about CO₂ footprint of different industries that is increasing the air pollution and causing many environmental problems. In construction industry, Portland cement (clinker) is being used as the main binder in concrete. Usually, normal concrete contain around 90% of clinker which is the main material that create CO₂, it generate around 0.81kg/kg of cement and requires a high energy by heating up to 1400 C° in order to produce cement [1]. Many researchers have done a lot of research to use SCMs (supplementary cementitious materials) mainly coal, fly ash and blast furnace slag in order to reduce the amount of clinker used in cement. However, some of these SCMs are found in limited amount or will increase the total cost of concrete. In the other hand, kaolinite clay is one of the materials that can be used in large amount to replace clinker and it's available in huge amount in nature. Kaolinite clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is a natural material can be found in in many place around the world with sufficient amount in order to replace large amount of clinker in cement which will lead to reduce the production of clinker and the emission of CO₂ [2]. In order to give the kaolinite clay a cementitious property, it need to be calcined by heating the clay up to 600–800 °C and the energy required for calcination is around half what is needed in order to prepare clinker [3].

1.1 Overview of limestone calcined clay cement (LC3)

The use of supplementary cementitious materials is one of the effective ways to reduce the emission of CO₂. Many studies have been done in order to test many types of materials that can be effectively used as cementitious materials such as fly ash and limestone but, some of these materials are found in nature in limited amount that can't cover the huge demand of cement all around the world or will increase the cost of cement [4,5]. Calcined clay was one of these supplementary material used and clay is available in the world in abundant amount and with calcination of the clay it can be used in substitution of the cement by maximum of 35% [6]. This substitution was made without affecting the cement properties and with the use of limestone the percentage of cement substituted increase by maximum of 60% to form limestone calcined clay cement (LC3) [7]. the percentage of substituted cement can vary from one mix to another, some study show that cement substitution can be 15% to 30% with additional of 10% to 15% limestone respectively [3,8]. Also studies show that there were a lot types of clay and only clay with kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) can be replaced after calcination to form metakaolin($\text{Al}_2\text{Si}_2\text{O}_7$) which have similar cementitious properties to normal cement thus it can be replaced with high amount [5]. LC3 in general will have similar strength as normal concrete with some improvement in durability aspect such as chloride diffusion and sulfate attack that is why this new type of concrete gets the attention of many researchers to reduce the CO₂ as well as improve the durability of concrete.

1.2 Significance of research

The significance of the research is to identify the locally available clays which can be promisingly used to partially replace clinker in concrete. This will enable the kingdom of Saudi Arabia to rely on local supplementary cementitious materials instead of importing fly ash and slag from abroad, which is the current practice. Following the durability properties will be investigate in detail which relatively a less explored area in LC3 concrete. This will add international significance to this research work.

1.3 Research objectives and scope

The prime objective of this study is to make LC3 concrete using locally available clays and investigate the durability properties of the LC3 concrete produced using these clays. The basic fresh and hardened properties of concrete will be measured as well to confirm the structural use of produced LC3 concrete. The specific objectives are:

1. To characterize the local clays in order to check their suitability for making LC3 concrete.
2. To check the fresh and hardened properties of the produced LC3 concrete.
3. Investigation of the durability properties of concrete (acid attack, chloride permeability, sulfate attack) mixtures prepared using the developed LC3 |

LITERATURE REVIEW

Several studies have been carried out to develop LC3 concrete. These studies show attention in many aspects for LC3 concrete such as morphology and microstructure, fresh and hardened properties, and on durability aspect of LC3 concrete. This study will focus on the important and recent development in this area.

The limestone calcined clay concrete (LC3) has a lower clinker as compared to normal concrete which the main factor to reduce the required energy for preparation for LC3 concrete this reduce of clinker will be replaced by metakaolin and limestone [5,8]. LC3 concrete have a higher water demand because of the nature of the calcined clay which is more finer than normal concrete with smaller pore size and lower permeability, this water demand will increase the water/blender ratio (w/b ratio) needed or can be replaced by super plasticizer [1,9]. LC3 have similar mechanical strength in compressive and flexural strength in comparison with normal cement with small difference. These difference can be in the amount of strength or in the time when the full strength gained [3,10].

2.1 Reaction mechanism of LC3

The phase of the microstructure of kaolin clays after calcination change from crystalline structure to amorphous structure and this will increase the reactivity of kaolin clay. This calcined clay will have a normal pozzolanic reaction with clinker but, with the presence of limestone, the carbonate available in limestone will react with alumina in the calcined

clay to form carbo aluminate phases. Carbo aluminate phases will potentially provide a denser microstructure with better strength and durability [11].

The hydration of the clinker phases when react with water will change Tricalcium Silicate (C_3S) and dicalcium silicate (C_2S) into calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). The more the C-S-H gel form during the reaction, the stronger and denser will be the concrete. The calcium hydroxide CH will react with aluminosilicates (AS_2) (which is present in pozzolanic materials) to form calcium aluminum silicate hydrate (C-A-S-H) [12].

In LC3 the presence of calcium carbonate (CC) will react with CH and AS_2 with water will form the carbo aluminate phases ($C_4A\hat{C}H_{11}$) this crystalline material will fill the structure and refine it to make better strength [11,13].

LC3 reaction can be described as a pozzolanic reaction were calcium hydroxide from CH and CSH gels (formed by cement hydration) are reacting with metakaolin to form CASH gels. Monocarboaluminate and hemicarboaluminate are aluminate species that formed in LC3 by the reaction of C_3A with limestone and portlandite this reaction generates more sulphate resulting to increase the ettringite amount. Additional hemicarboaluminate can be formed by the reaction of metakaolin with CH and calcium carbonate [14,15].

2.2 Microstructure of LC3

The morphology was studied in order to find the microstructure and to find what the main minerals that kaolinite clay constructed of and to have more understanding to make correlations between kaolinite chemical composition that give LC3 its properties [14].

A study has studied the microstructure through Scanning electron microscopy (SEM), reaction product and pore structure of paste specimens. By using X-ray diffraction (XRD) the main component of calcined clay was SiO_2 , Al_2O_3 and Fe_2O_3 also by measuring the partial size distribution it shows the LC3 is finer than normal cement. In thermogravimetric analysis (TGA) when the temperature was increased from 20 to 300 °C the water completely evaporated. The dehydration of portlandite happens in 400 to 500 °C. In the mesoscopic image when the sample heated to 300 °C the color become lighter and some micro cracks appear but with increase the heat to 900 °C the cracks increase to 150 μm . The pore size distribution becomes finer because of the further hydration the anhydrous binder from 20 to 300 °C. When the temperature reach more than 550 up to 900 °C the dense structure becomes gradually destroyed [12,16].

Another study shows that LC3 have decreased the formation of CASH and CH which mean the LC3 reaction is pozzolanic like reaction. LC3 react with CH to form CASH amorphous gels with gypsum to form more CH. LC3 reaction reduce the C_3S , C_2S and tetracalcium aluminoferrite (C_4AF) but, with more illite quartz and calcite coming from calcined clay and limestone the formation of CASH still the same [17].

Another study had tested XRD on 28 days reaction. This study shows a sharp decrease on portlandite (CH) at $2\theta=18^\circ$ between LC3 and OPC mix. This decrease was due to the

reaction between metakaolin and CH. Also, this study has tested the samples with TGA analysis. The decrease in weight has divided into 3 ranges : First range were the CSH gels, aluminate ferrite mono-sulfate and hydration product are dehydrated between 50 and 400 °C, second range is the de-hydroxylation of portlandite between 400 and 500 °C, and last range between 550 and 950 °C where the de-carbonation of calcite occur [18].

2.3 Fresh properties of LC3

Limestone calcined clay concrete (LC3) fresh properties can be tested using the same methods used for normal concrete. Clay particles required more water in order to keep the same workability of normal concrete. For LC3 with 0.40 to 0.45 water to binder ratio give comparable results with normal concrete with the usage of superplasticizer. The saturation dosage required for LC3 is greater in compare for normal concrete. Bleeding was observed when high dosage of superplasticizer been used. The viscosity for LC3 is higher than normal concrete. Slump test achieves 190mm when 0.65% superplasticizer used by weight of cement [1].

This study concludes that with using 50% clinker, 30% calcined clay, 15% lime stone and 5% gypsum there will be higher need for superplasticizer in order to achieves similar workability and fluidity for LC3. With water to binder ratio lower than 0.40 the demand for superplasticizer increases in order to achieve similar slump test result. With water to binder ratio of 0.3 the increase in superplasticizer was 1.6% by weight of cement and the goal slump result was not achieved [1].

Another study says that metakaolin have average smaller practical size as clinker but, larger than silica fume. Duo to the fines of metakaolin the mixing time has increased to perform a good mixed concrete. Also the setting time were decreased in LC3 with 10% to 20% replacement because of reduction of free water which been absorbed by the clay and the additional gypsum maybe a factor for decreasing the setting time [17].

2.4 Mechanical strength of LC3

Mechanical strength for concrete is important in order to know the capacity for the final product to carry loads and determine if the concrete will be able to be used in construction. One of the most important mechanical properties is the compressive strength of concrete. There are many studies that test the compressive strength of LC3 concrete with different LC3 mix in order to find the closest LC3 to the normal concrete.

One study has used a mix with 50% clinker, 45% limestone calcined clay and 5% gypsum and another mix with 70% clinker and 25% limestone calcined clay and 5% gypsum with water to blender ratio (W/B) of 0.55 for both mixtures. The compressive strength was measured for both mixtures at early age 1-3 day and in the 7-day and at maximum strength in 28 days. The evolution of compressive strength was the highest at 1 to 7 days (around 75%) then the increase in the strength increased slowly to the 28 days (around 25%) after that the increase in strength was very small. The mixture with 70% clinker show a higher early strength compared to the 50% clinker because the clinker increase the early strength but, both ended at 28 day with similar strength [3,4].

Another study tested the compressive strength with carbonation cured for LC3. This study has used 4 curing times first samples were cured for 24 hours second samples were cured for 30 hours. The third sample were cured for 14 days and the last samples were cured for 28 days. The first 3 samples with 30% limestone calcined clay has a compressive strength of 47 MPa and the same 3 samples but, with 45% calcined clay have 40 MPa compressive strength at 28 day. Carbonation curing shows increase in the compressive strength more in the normal cement but, with the increase of limestone and clay content the increase of the strength was affected by the carbonation curing and decrease the amount of increasing in the compressive strength in higher replacement level compared with clinker samples so, the final compressive strength was lower as the calcined limestone clay increase under carbonation curing [19].

Another study tested compressive of LC3 in comparison with OPC and fly ash concrete FA30 with cement grade of M30 and M50. Also, common mix C-mix. The water to binder ratio was between 0.4 to 0.6. The compressive strength was tested at 3, 7, 28, 90 and 360 days. The result shows the compressive strength of LC3 were comparable with OPC but, FA30 had a lower strength compared to OPC and LC3 at early ages. LC3 and FA30 show a good increase in strength at later age more that the OPC. Also, they studied the modulus of elasticity of these three mixtures and show that for OPC, LC3 and FA30 the modulus of elasticity was similar in all cement grades used. The autogenous and drying shrinkage were tested in these mixes and show that LC3 had the lowest shrinkage among the three mixtures [10].

Another study has used 10% and 30% replacement of LC3. The study reported a decrease in strength of LC3 mixtures caused by the increase of the macro-pores and low content of hydration in LC3 samples [17].

2.5 Durability aspects of LC3

One of the advantages of using LC3 is the improvement happen in durability in chloride penetration and diffusion also in sulfate attack. One study showed that calcined clay promotes the hydration by decreasing the time and the period required for sulfate to deplete. The time for sulfate depleting is set by SO_3 , which make sulfate delayed by the increase in SO_3 content [3].

Another study show that a rapid chloride penetration test (RCPT) was tested on LC3, normal concrete and concrete with 30% fly ash was measured on order to see the improvement in LC3 concrete. The sample tested at 28 and 90 days. The result showed that LC3 had the minimal charge passed at both durations. This improvement was because of the difference between the hydration products between these three concrete types [10].

Another study made on chloride diffusion. This study use 7 types of concrete 2 normal concrete with different binder to water ratio (0.5 and 0.4) and 2 concrete with fly ash with (0.45 and 0.35) binder to water ratio and 3 LC3 concrete with (0.5, 0.45 and 0.4) binder to water content. The result show that normal concrete has highest rate of chloride ingress in both case duo to less porous microstructure and the high ionic resistance in comparison with concrete with fly ash and LC3. Also, LC3 show similar to lower chloride diffusion than concrete with fly ash in all cases measured at 56 days [4].

A study showed that the LC3 concrete have a lower calcium content compared with normal cement and other blended cement type. This lower calcium content will affect the capacity to bind CO_2 and will decrease the carbonation resistance for LC3. The test was mad indoor and outdoor and in both case LC3 was lower than normal concrete using phenolphthalein solution [5].

RESEARCH METHODOLOGY

3.1 Clay preparation

3.1.1 Collection of clay

In order to make LC3 concrete, finding a good amount of clay is needed that contain reasonable amount of kaolinite in order to have the cementitious property for this task. A local ceramic factory was visited that have kaolinite clay (since kaolinite clay is a major material in ceramic work) and 3 clay samples were collected, namely white local clay and local yellow clay (from Al-Kharj), Ukrainian white clay. These clays need to be justified to have kaolinite amount to be suitable for making LC3 or not. In order to find the minerals composition of the clay sample, X-ray fluorescence (XRF), XRD and TGA were conducted to know the difference in each type of clay and to know the amount of kaolinite in these clays. The samples were grinded manually to pass sieve 200 with particle size of 75 μ m. XRD was tested using Mini-Flex 600 made by Rigaku company. The instrument was running 40kV with 15mA. The scanning speed was 5.00°/min with step width of 0.05°. the scanning range was between 5 ~ 65°. TGA was tested using SDT-Q 600 made by TA-instruments. The temperature was raised from 50 to 900 C° at rate of 10 °C/min. Nitrogen gas was used to provide less reactive atmosphere with rate of 100 ml/min. The kaolinite to metakaolin conversion takes place between 400 to 600 °C. Hence, the weight loss in this range indicates the percentage of kaolinite in each type of clays.

3.1.2 Clay crushing and calcination

The clays samples collected were in lumps form and needed to be crushed using crushing machine in order to get a clay that pass sieve 150 μm . a crushing machine were used in order to crush the lumps of clay into power as shown in figure (1). The crushing mechanism was done into multiple cycles of crushing and sieving to get the fine clay powder with the required amount in this study for each type of clay ash shown in figure (2). Calcination of kaolinite clay done be by heating the powder clay sample using calcination furnace up to 850 $^{\circ}\text{C}$ in order to change the kaolinite clay to metakaolin to have the cementitious ability. The calcination were up to 850 ($^{\circ}\text{C}$) using Linn High Therm stationary furnace (Melting furnace HT series). as shown in figure (3) and the temperature were monitored to not exceed 900 ($^{\circ}\text{C}$) to prevent unreactive mullite crystals [20,21]. The clay samples were put in steel plates (600 to 800 g for each plate) then placed inside the furnace. The maximum capacity for the furnace were 6 plates only duo to the small size of the furnace. The furnace heating rate was 10 $^{\circ}\text{C}/\text{min}$ so, it takes around hour and half to get to the desired temperature. The samples were kept for 2 hours in fixed temperature of 850 $^{\circ}\text{C}$ in order to make proper calcination for all the kaolinite in the clay.



Figure 1 Crusher machine



Figure 2 Sieving Machine



Figure 3 Stationary Furnace



Figure 4 Samples inside furnace

3.2 Materials

3.2.1 Portland cement

Portland cement type I was used to prepare the LC3 mix, it was provided by the ready-mix plant after it was tested to pass through the ASTM C150.

3.2.2 Limestone powder

Limestone powder was collected from a gypsum work warehouse. The limestone was in powder form after passing through sieve #200.

3.2.3 Gypsum

Gypsum was provided by a ready-mix plant after it was tested to pass through the ASTM C471M.

3.2.4 Fine aggregate

Dune sand was used as fine aggregate used in the construction mortar and concrete specimens. The sand fineness modulus was 1.85 and its specific gravity at dry condition was 2.55. the absorption of sand was 0.58%.

3.2.5 Coarse aggregate

In LC3 mix the coarse aggregate size were fixed to have the same distribution in all mixes.

The coarse aggregate size distribution is showed in table 1:

Table 1 Coarse aggregate size distribution

Aggregate size	Size (mm)	Size (in)	% from total aggregate
1	9.525	3/8	40
2	4.7625	3/16	50
3	2.38125	3/32	10

3.3 Select appropriate mix based on literature studies and criteria

3.3.1 Mix design

In the previous studies, there were different mixes used in LC3 and that difference was in the percentage of clinker to calcined clay. Most of the studies used mixture of 50% clinker, 5% gypsum and 45% clay and limestone (2:1) LC50 (50% the replacement of clinker). The other mixture used was 70% clinker, 5% gypsum and 25% clay and limestone (2:1) LC30 (30% the replacement of clinker). In this study, both mixes had studied to see the difference on the strength and durability change for both mixtures and one more mix LC70 (70% the replacement of clinker) have been added with 30% clinker, 5% gypsum and 65%

clay and limestone (2:1). These three mixtures had been applied in the three clay types WC, UC and YC. These mixtures will include paste, mortar and concrete samples to do multiple tests to have a general idea of the behavior of LC3. In all these mixtures, all the changes have been minimized in order to make the main comparison factor are the clay types and replacement. In order to do that, all mixture had the same casting methods and environment. All curing method was the same and all mixture components were the same. Water to binder ratio (W/B) was 0.4 (except for normal consistency, setting time and flow table tests W/B will be explained in fresh properties in details) for all mixtures and the binder content was 400kg/m³. The amount of superplasticizer (SP) will be different to control the workability of the concrete. These mixes proportioning is explained in table (2):

Table 2 Mix design for 30% clay replacement

Mix ID	Clay type	OPC (%)	Clay (%)	LSP (%)	Gypsum (%)	SP (%)
CM	-	100	0	0	0	0.17
WC30	White	70	16.5	8.5	5	1.5
WC50		50	30	15	5	1.5
WC70		30	43.5	21.5	5	1.5
UC30	Ukrainian	70	16.5	8.5	5	1.5
UC50		50	30	15	5	1.5
UC70		30	43.5	21.5	5	1.8
YC30	Yellow	70	16.5	8.5	5	1.5
YC50		50	30	15	5	1.65
YC70		30	43.5	21.5	5	2.2

Superplasticizer content were different from mix to another in order to achieve workable concrete (slump 100 to 200) mm with the same W/B ratio of 0.4 for all mix. An aqueous solution of modified polycarboxylates (co-polymers) based superplasticizer was used from Sika. The super plasticizer was added to the water then to the dry mix.

3.3.2 Specific gravity

The specific gravity of the calcined clays was measured using the Le Chatelier flask. To measure the specific gravity. First, filling the flask with kerosene until the reading is 0. Then, adding 50 grams of the calcined clay powder in the flask and shake it properly to make sure all the clay go down and be completely submerged with kerosene. Now, the new reading after adding the clay can be taken. To find the specific gravity, divide the 50 grams to the new reading (different between initial reading (0) and the new reading) and the result will be the specific gravity of the clay. The set up for measuring the specific gravity is shown in table 3



Figure 5 Specific gravity test setup

The specific gravity of the clays is as following in table

Table 3 Specific gravity for calcined clay

Clay	Specific Gravity
White clay (WC)	2.5
Ukrainian clay (UC)	2.49
Yellow clay (YC)	2.7

3.4 Fresh properties

Fresh properties for LC3 tested were including the following tests: normal consistency, setting time, flow table tested on paste and a slump test for concrete.

3.4.1 Normal consistency

In normal consistency the target is to find the optimum W/B ratio. This W/B ratio can be found when the 10mm needle penetrates the paste sample for 10mm of the vicat plunger. The test was performed in a lab condition where temperature around 25 ± 2 °C. The W/B ratio started with 0.3 then increase or decrease according to the reading of the vicat reading. With every change of W/B ratio a new paste were prepared and when the reading goes above and below 10 mm interpolating of the value were taken at exactly 10 mm penetration and found the optimum W/B ratio. All steps for this test were following ASTM 187 [22].

3.4.2 Setting time

Setting time was the following step after getting the optimum W/B ratio in normal consistency. In this test both initial and final setting time were measured. The initial setting time is when the 1mm needle penetrates the paste sample for 25 mm and the final setting time is when the 1 mm needle does not penetrate the sample surface. This test were performed in lab conditions and all steps were following ASTM191 [23]. The setup of the test is shown in figure 6.



Figure 6 Normal consistency and setting time setup

3.4.3 Flow table

Flow table test was the last step for paste fresh properties tests. In this test, W/B ratio was the same that had been found in normal consistency. The test was performed in lab condition with temperature of 25 ± 2 °C. The flow table was cleaned properly in order to prevent any error in the flow of paste for each trial and each mix. The paste was tamped for 20 time at each layer of 25 mm thickness (total thickness of the sample is 50mm). After removing the ring mold, the sample were dropped for 25 time within 15 second then the spread of the paste was measured in both diagonal dimensions to find the paste flow. the test was following ASTM 1437 [24].

3.4.4 Slump test

In concrete mixes, a slump test was performed to know its workability. The test was directly after the end of mixing the concrete using concrete mixer. Slump test were

controlled by using SP in order to get good workable concrete without changing the W/B ratio. The desired slump was between (100 - 200) mm. before starting the test, all equipment for the slump test were cleaned properly in order to prevent any effect of the results. The slump cone were filled into 3 layers and with each layer, a 25 tamps using a tamping steel rode. The tamps were distributed all around the sample. A tap measure was used to find the drop of the slump after removing the cone. The test were following the ASTM 143 [25].

3.5 Mechanical Properties

Mechanical properties for LC3 tested were including the following tests: compressive strength, modulus of elasticity and shrinkage.

3.5.1 Compressive strength

Compressive strength is one of the main properties that describe the quality of concrete. In this work compressive strength were tested for concrete, mortar and paste with different durations and different sample size as shown in the following table 4:

Table 4 Compressive strength sample and durations

Sample	Size (mm)	Duration	Standard
Concrete cylinders	75*150	7,28,90 days	C39
Concrete cubes	50*50*50	28,90 days	C109
Mortar cubes	50*50*50	7,28 days	C109
Paste cubes	25*25*25	7,28,90 days	C109

The compression rate was fixed for all the tests of 1.5KN/s. all samples were cured under water the test was taking place after removing the sample from water and wiped with clean cloth in order to be tested in saturated surface dry (SSD) condition. For cylinders samples, the top and bottom surface were grinded using a grinding machine to make the testing surface smooth and completely horizontal to make the load have a good distributed load along the length of the sample. While in cube samples, the testing surface were any smooth surface at the sides of the cube (excluding the top surface). All compressive strength test were following ASTM C39 for cylinders and ASTM C109 for cubes [26,27]. The compression testing machine is shown in figure 7.



Figure 7 Compressive strength for cubic samples

3.5.2 Modulus of elasticity

Modulus of elasticity test were taking place at the same time of testing the compressive test for cylindrical samples. To measure the change in length, a set of 2 LVDTs and rings

were fixed into the sample to read the change in length between the two rings (gage length of 75 mm). An average measurement was taking for the LVDTs and the reading was connected with the load using load cell. These entire components were connected using a data logger to take an automatic reading for each second. Every time the sample was checked to be fixed properly in order to prevent any miss reading for the change in length the test were following ASTM C469 [28]. The set of testing is shown in figure 8.



Figure 8 modulus of elasticity measuring setup including load cell, 2LVDTs and holding rings connected to data logger

3.5.3 Shrinkage

Shrinkage was tested in mortar samples of length 250 mm and 25*25 mm cross-section. After the demolding, an initial measure for all shrinkage samples was taken as a reference measurement. The samples then were kept under water for 28 days then samples were taken out of water to dry then the shrinkage reading started. At first week, 2 measuring were

taking every day, then the second week a measuring was taking once a day, and then a 2 reading were taken in the third week forward until the 70 days shrinkage. The shrinkage was measured using LVDT connected to a data logger with a brass bar used to calibrate the LVDT before measuring the samples. The samples were measure in $\text{mm} \times 10^{-4}$ to get an accurate measurement. The test measuring was following ASTM C596 [29].

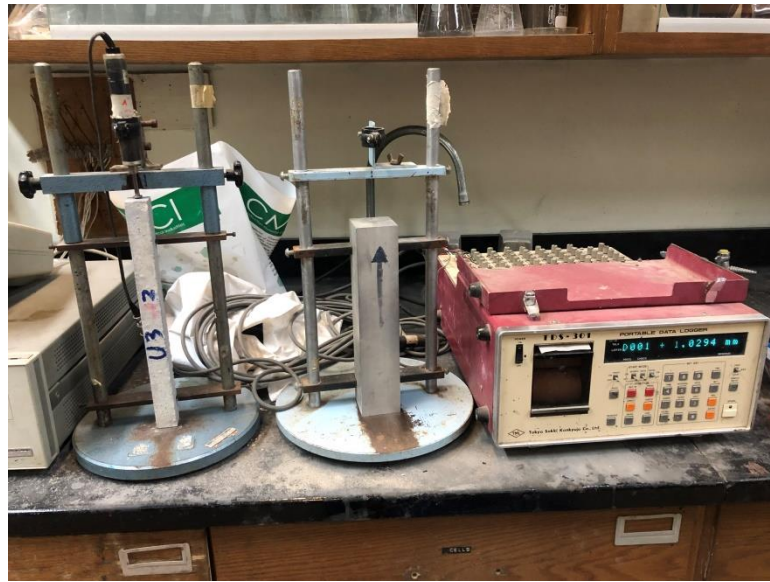


Figure 9 Shrinkage test setup including data logger and LVDT

3.6 Durability Properties

Durability properties for LC3 tested were including the following tests: rapid chloride permeability test (RCPT), chloride migration, sulphate and acid attack. These tests were obtained to compare between CM and LC3 against permeability and exposures. All samples were tested after 28 days curing under water.

3.6.1 Rapid chloride permeability test

RCPT is measure the ability for chloride to penetrate the concrete surface and give a qualitative result depending on the number of columns have passed the sample. The samples were a 100 mm diameter disk with thickness of 50 ± 2 mm. the disk were coated by epoxy coating in order to make the chloride move in one direction. The disk was prepared from a (100*200) cylindrical sample. A cutting saw were used to cut the samples into 50 ± 2 mm thickness then coated by the epoxy coating as shown in figure 12. After the epoxy coating get dry, the samples were kept in a water tank in order to make the samples fully saturated and to remove all air bubbles inside the samples. The water tank was provided with air pump to make the tank empty from the air for 2 hours. The air pump then switched off but, the tank still closed so the samples still under vacuumed environment for the next day (24 hours). The next day, the samples were removed from the water tank and placed in to RCPT cell. The cell have two sides, first side will be filled with NaCl solution with a concentration of 3% by mass. The second side will be filled with NaOH solution with 0.3 molar (0.3N). Both solutions were prepared using distilled water. Then, the cell was fixed properly in order to prevent any leaking of the solution. After that, the cell were connected to Prove It device (to measure the RCPT) and connected to computer. The NaCl solution was connected to the negative cable and the NaOH solution were connected to the positive cable. The potential difference between the solutions was 60 V and the test duration was 6. The test were following the ASTM C1202 [30]. All cells were having a cooling fin to prevent overheating.



Figure 10 Concrete disk of 50 mm thickness before epoxy coating



Figure 11 Concrete disk of 50 mm thickness after epoxy coating

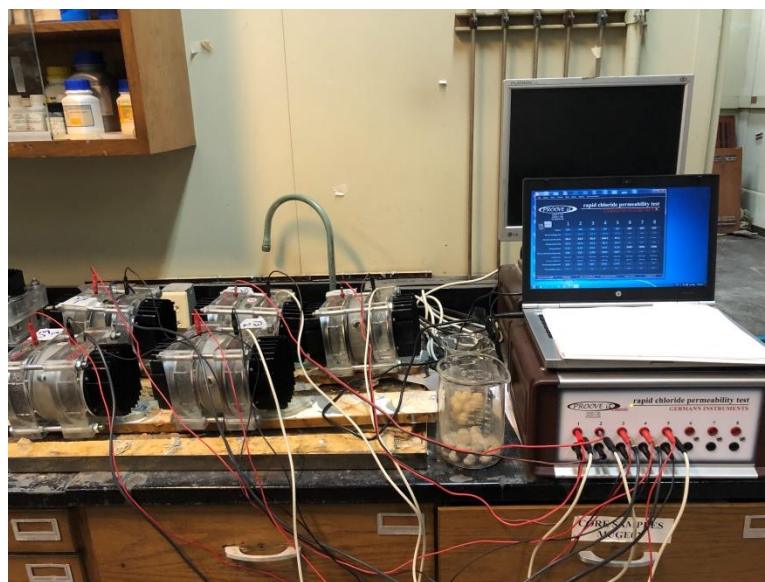


Figure 12 RCPT testing set (cells are connected to DC device with computer).

3.6.2 Accelerated chloride migration test

The accelerated chloride migration test also measures the penetration of chloride in concrete sample. Also, it shows the penetration depth for where the chloride has reach into the sample. By this result the non-steady state chloride migration coefficient can be estimated. This result can give the rate of the chloride penetration per unit of time based on the initial and final current and voltage applied. The sample preparation is the same of the RCPT test the difference is that the sample will be vacuumed under a saturated solution of calcium hydroxide $\text{Ca}(\text{OH})_2$. Also the solution concentration was 10% for NaCl and 0.3N for NaOH. The initial potential deference is 30V and the test should run just to give an initial reading for the current. From that initial current reading, a new potential difference will be applied depending on the value of the current with 30 V from table 1 in the NTB 492 standard. Also, the test duration will be determined depending on the initial current results the duration may vary from 6 hour to 96 hours. After applying the new potential defiance the new current will be recorded an also the initial temperature. At the end of the test, the final temperature reading will be taken. After the end of the test, the sample should be cutter in half using cutting saw then sprayed by silver nitrate (AgNO_3) solution with concentration of 0.1 N to show the depth of penetration. The region where the chloride penetrates will be shown in white color after reacting with the silver nitrate. The total thickness of the sample and depth of penetration should be measure with the addition of the initial and final potential deference, current and temperature in order to calculate the non-steady state chloride migration coefficient using the following equation [31]:

$$D_{nssm} = \frac{0.239(273 + T)L}{(U - 2)t} \left(x_d - 0.0238 \sqrt{\frac{(273 + T)Lx_d}{U - 2}} \right)$$

Where:

D_{nssm} : the non-steady state chloride migration coefficient, $\times 10^{-12} \text{ m}^2/\text{s}$;

U : absolute value of the applied voltage V ;

T : average value of the initial and the final temperature in the anolyte solution $^{\circ}\text{C}$.

L : thickness of the specimen, mm .

X_d : average value of the penetration depth, mm

t : test duration, hour.

3.6.3 Sulphate attack

Sulphate attack was tested in concrete cubes (50*50*50) mm and in paste cubes (25*25*25) mm. The samples were cured under water for 28 days before the exposure to sulphate. Sulphate solution had a concentration of 5% (2.5% sodium sulphate and 2.5% magnesium sulphate). The container had solution to samples ratio of 5:1 by volume to make sure that the amount of solution is sufficient for the samples. The spacing between samples was 2.5 to 3.8 cm (1 to 1.5 inch) so the solution will surround the samples from all sides as shown in figure 13. The samples will be tested in 2, 4 and 9 months. In each testing interval the samples were measured in weight loss, compressive strength and change in appearance. The containers were kept in lab condition with temperature of $25 \pm 2 ^{\circ}\text{C}$. The test will follow the ASTM C1012 [32]

3.6.4 Acid attack

Acid attack was tested in concrete cubes (50*50*50) mm and in paste cubes (25*25*25) mm. The samples were cured under water for 28 days before the exposure to Acid. Acid solution had a concentration of 3% sulfuric acid. The container had solution to samples ratio of 5:1 by volume to make sure that the amount of solution is sufficient for the samples. The spacing between samples was 2.5 to 3.8 cm (1 to 1.5 inch) so the solution will surround the samples from all sides as shown in figure 13. The samples will be tested in 2, 4 and 6 months. In each testing interval the samples were measured in weight loss, compressive strength and change in appearance. The containers were kept in lab condition with temperature of 25 ± 2 °C. The test will follow the ASTM C1898 [33].



Figure 13 Sulphate and acid samples arrangement in the solution

RESULTS AND DISCUSSION

4.1 Microstructure of raw clays

4.1.1 XRD of raw clays

The collected clay samples were crushed into 75 μm in order to perform XRD analysis test to know the component of the collected clay samples. XRD was tested on the three clay types WC, UC and YC to identify the kaolinite peaks and see the change after the calcination process. XRD for raw clays is shown in figure 14.

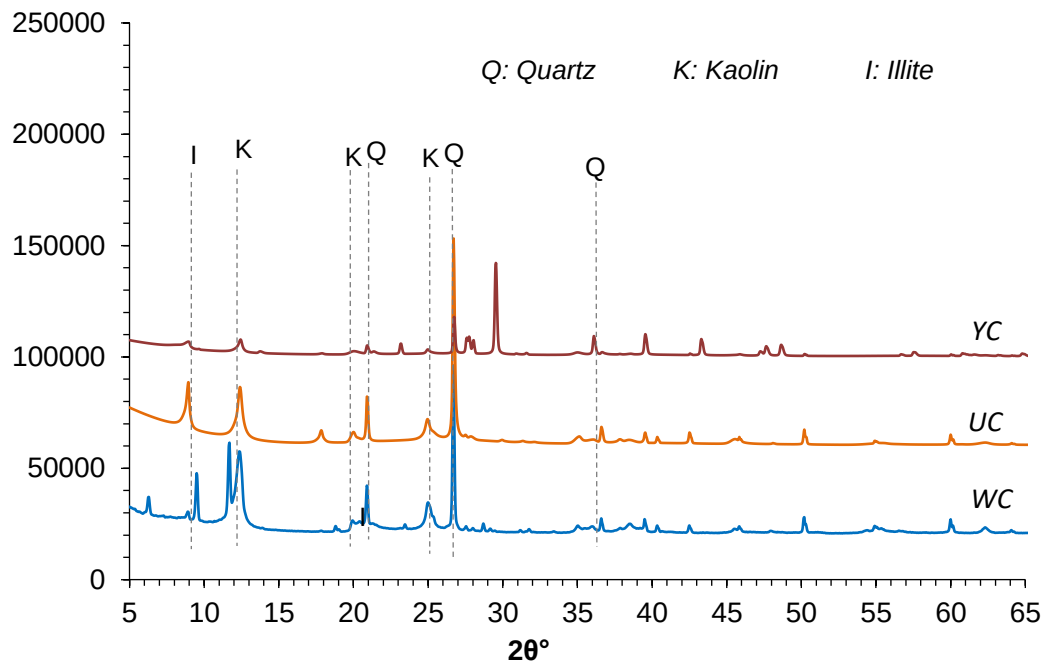


Figure 14 XRD analysis for the 3 raw clay samples. Q-quartz, K- kaolin, I- illite

XRD graph shown the main peaks are kaolinite and quartz in both WC and UC but in yellow clays, the amount of kaolinite and quartz is less which may affect the cementitious ability when yellow clay mixed with cement. Similar result were found in Hassan T study

as the clay were tested in that study have greater SiO_2 and Al_2O_3 (which mainly found in kaolinite) ratios in white clay more than the other types of clays that were included in his study [8]. This result of XRD is before calcination and it's expected for the kaolinite peaks to disappear or to form a hump after the calcination where the kaolinite will change into metakaolin.

4.1.2 TGA of raw clays

TGA analysis was tested to see the drop on weight for each clay sample in order to find out the kaolinite content. DTG graph show the reverse 'V' peak between 400 to 600 °C which is the region associated with the de-hydroxylation of kaolinite and formation of metakaolin [18].

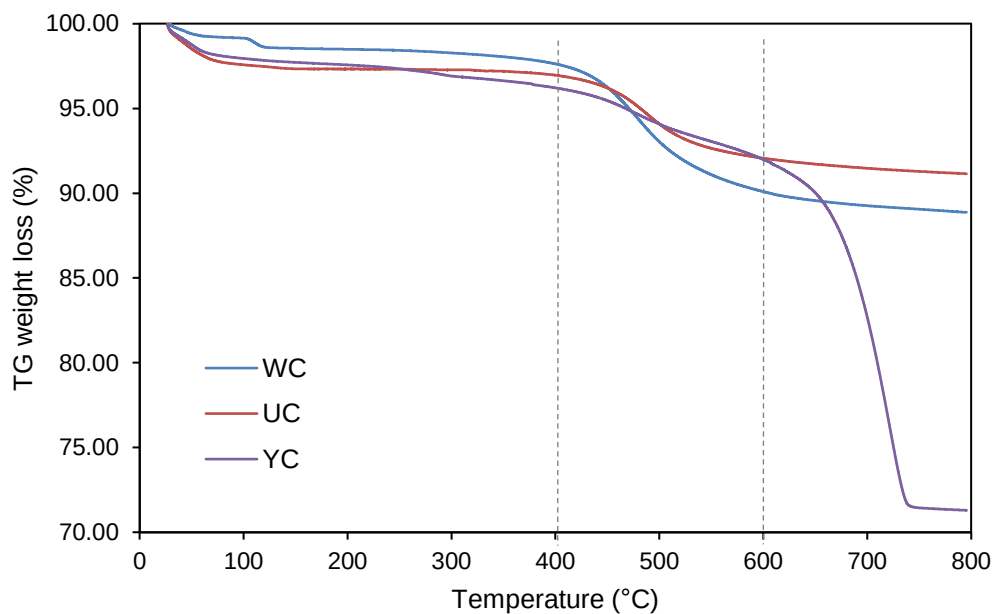


Figure 15 TGA for temperature (°C) and weight loss (%).

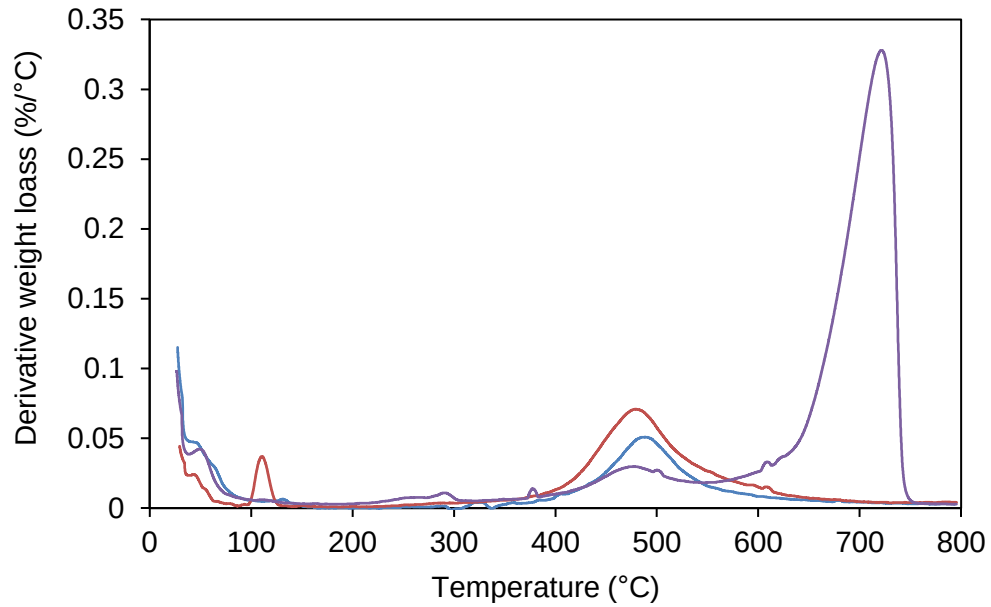


Figure 16 : DTGA for temperature (°C) and derivative weight loss (%/°C)

The DTG graph shows the weight loss cause by the change of kaolinite into metakaolin mainly between the temperatures of (400-600) °C in figure (3). This chart of TGA show the temperature and weight loss in percentage the amount to kaolin can be found in each type of clay by taking the loss between 400 and 600 °C. The kaolinite content can be calculated using the following formula[34]

$$Kaolinite\ content\ \% = \frac{\Delta\ sample\ weight\ loss\ \% (400 - 600)^{\circ}C}{14} \times 100$$

By using this equation, the amount of kaolinite in this clay can be summarized in Table 9:

Table 5 weight loss (%) for TGA

Clay type	Temperature range	Weight loss in %	Kaolinite content %	Weight loss in %
WC	400-600	5.15	53.77	8.755
UC	400-600	3.55	35.40	5.812
YC	400-600	2.4	30.16	24.9

From these results can see the amount of kaolinite ranged between 53% and 30% between different clay types which can be medium to low kaolinite content.

4.2 Microstructure of calcined clays

After the calcination process, another XRD and TGA test were conducted with addition of XRF to check the efficiency of the calcination process to change the kaolinite into metakaolin and to see what oxides have formed in the clay after calcination.

4.2.1 XRF of calcined clays

XRF were tested on the calcined clay, limestone powder and gypsum in order to obtain the chemical characteristics of each component. This test was performed to have an idea of what component will form in the hydration reaction of LC3. The results of XRF are shown in table 10 for component and in table 11 for minerals

Table 6 XRF material component for LC3 clays, limestone and gypsum

Material	Chemical component in percentage %								
	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	FeO	NiO	SO ₃
WC	0.21	28.65	59.45	0.36	0.64	3.83	6.86	-	
UC	-	28.78	62.97	2.51	0.44	2.13	2.55	-	
YC	0.88	10.18	24.79	0.99	47.06	1	15.1	-	
LSP	7.44	-	14.40	-	77.80	-	0.33	0.03	
Gypsum	0.78	-	-	-	57.72	-	0.21	-	41.30

Table 7 XRF minerals component for LC3 clays, limestone and gypsum

Material	Minerals in percentage %										
	O	Mg	Al	Si	K	Ca	Ti	Fe	Ru	Ni	S
WC	48.54	0.12	15.16	27.79	0.30	0.45	2.3	5.33	-	-	-
UC	49.06	-	15.23	29.43	2.09	0.32	1.28	1.99	0.6	-	-
YC	35.70	0.53	5.39	11.59	0.82	33.63	0.6	11.74	-	-	-
LSP	32.9	4.49	-	6.73	-	55.60	-	0.26	-	0.03	-
Gypsum	41.58	0.47	-	-	-	41.25	-	0.16	-	-	16.54

From XRF result, WC and UC were having similar chemical composition. The main oxides are Al_2O_3 and SiO_2 which make almost 90% of WC and UC composition which it similar to what have been reported in Duo Zhang study [35]. YC clay are mainly have SiO_2 and CaO were Al_2O_3 as secondary oxides and contain 10% of YC. Also the SiO_2 in YC is half the amount available in WC or UC which related to less kaolinite content. The YC clay also having 15% FeO which is higher than the amount in WC and UC. Which can related to the yellow color of raw YC and reddish color of calcined YC as reported in Anjaneya Dixit study [18].

4.2.2 XRD of calcined clays

XRD patterns in figure of the calcined clay show that the kaolinite peaks have disappeared which related to reduce in kaolinite crystals and the formation of amorphous metakaolin after the calcination process. Similar result were show in Rodrigo Fernandez study as

showing the drop of kaolinite in comparison with illite and montmorillonite as the kaolinite have a high decomposition while the other have smaller compared with kaolinite [21]

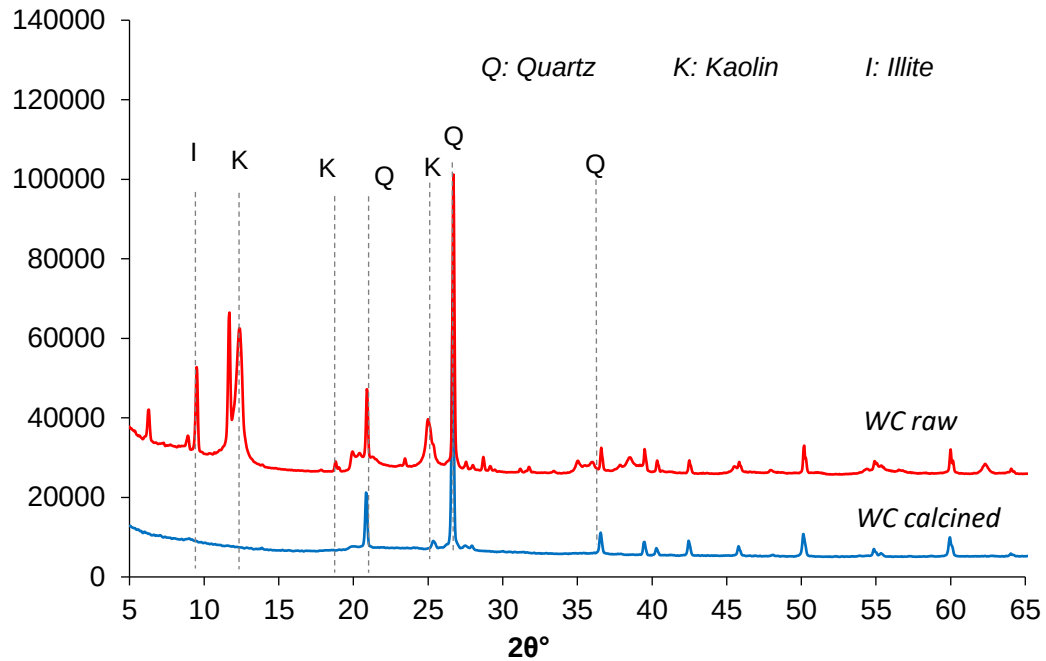


Figure 17 XRD comparison between raw and calcined clay before and after calcination for WC.

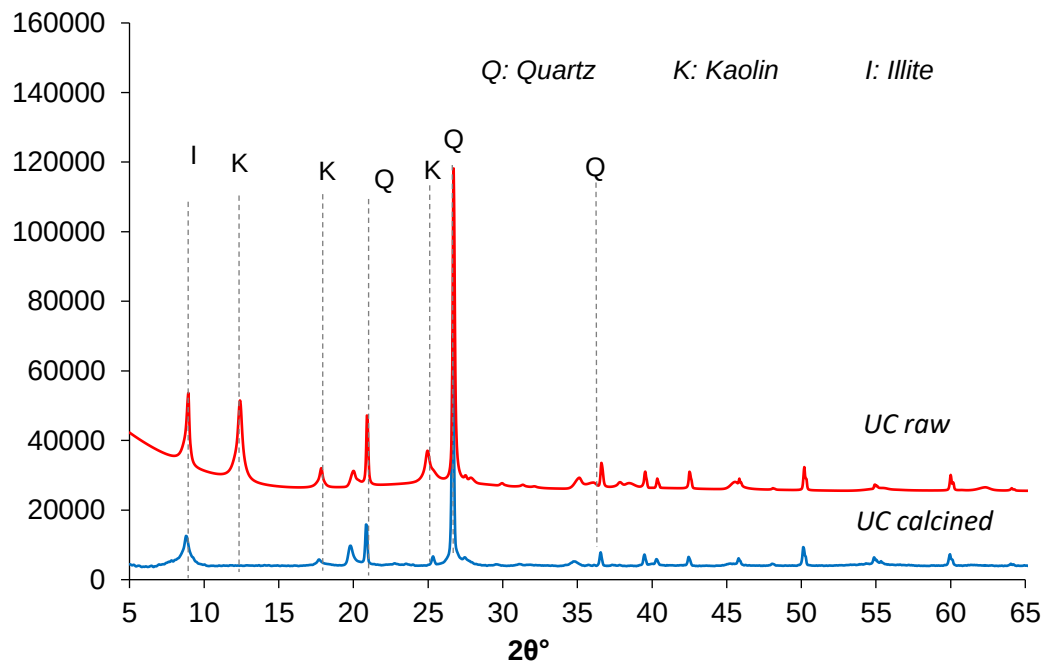


Figure 18 XRD comparison between raw and calcined clay before and after calcination for UC.

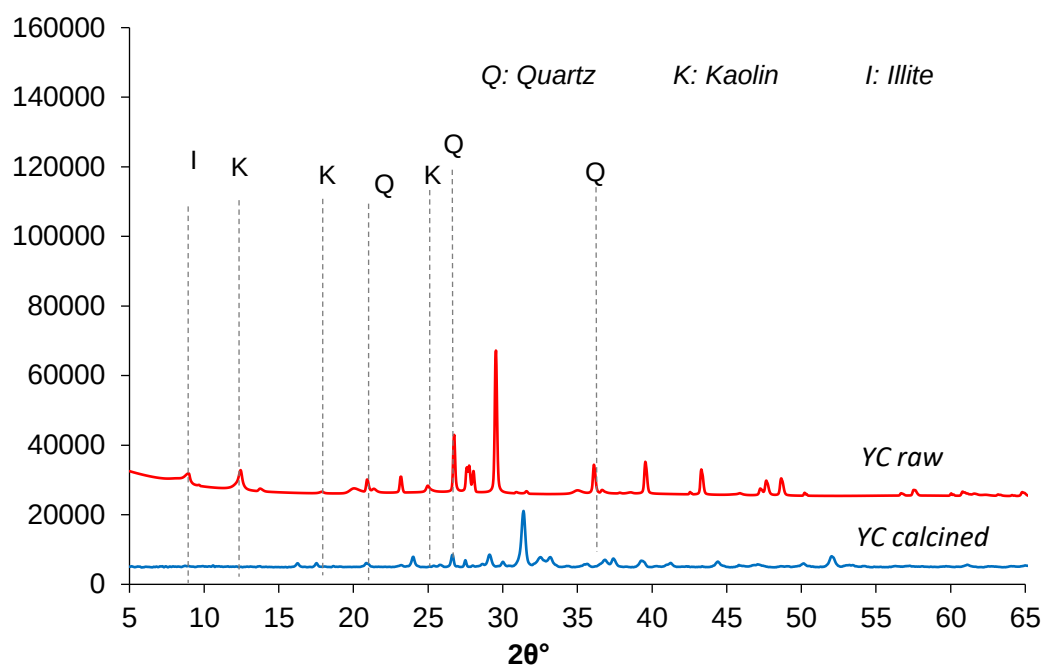


Figure 19 XRD comparison between raw and calcined clay before and after calcination for YC.

4.2.3 TGA of calcined clays

TGA analysis show that before and after calcination, the drop in weight loss between (400-600) (°C) have completely disappear which mean there is no kaolinite have changed into metakaolin duo to the calcination process and show that the calcination were efficient as shown in figure.

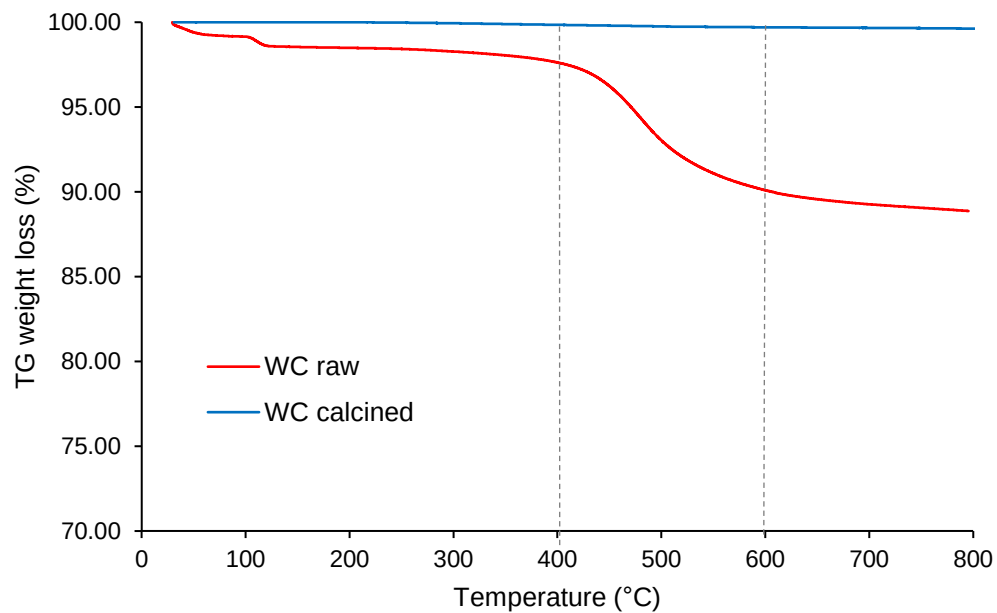


Figure 20 TGA comparison between raw and calcined clay before and after calcination for WC.

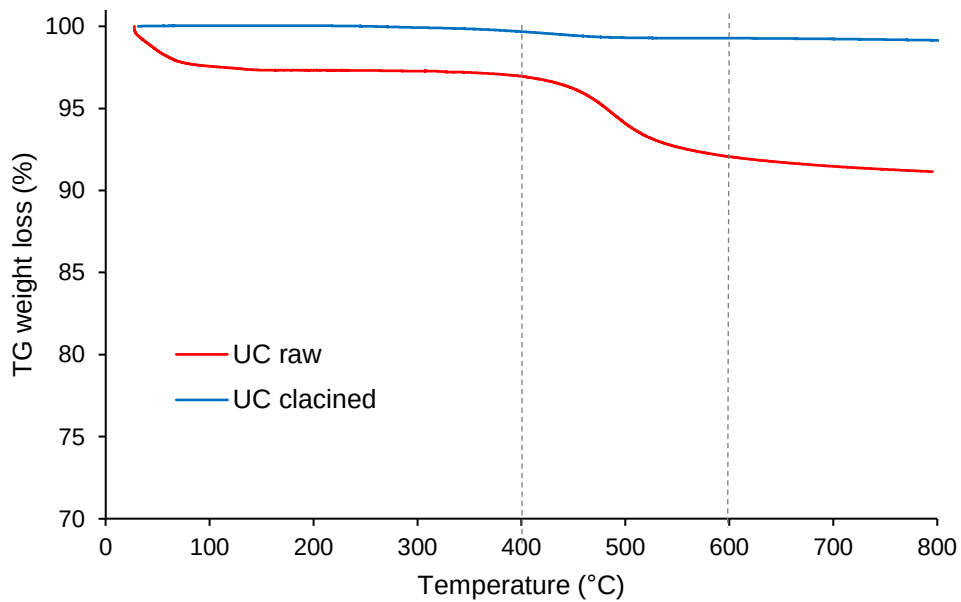


Figure 21 TGA comparison between raw and calcined clay before and after calcination for UC

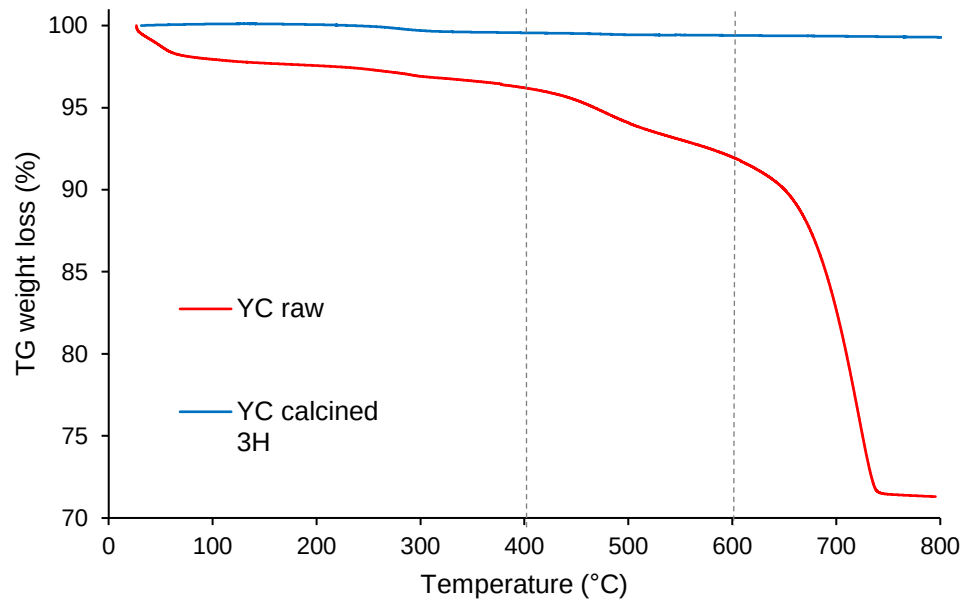


Figure 22 TGA comparison between raw and calcined clay before and after calcination for YC

4.3 Fresh properties results

4.3.1 Normal consistency

Normal consistency aimed to get a 10 mm penetration through paste mixes using the 10 mm needle. The results for the normal consistency are showed in the following figure 23:

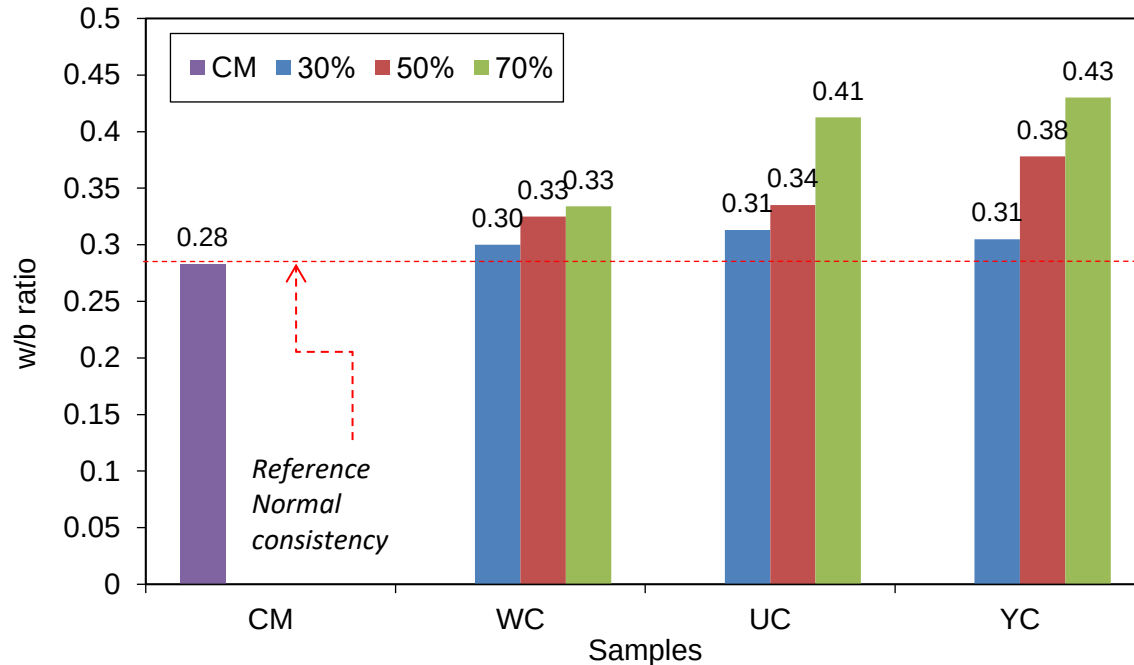


Figure 23 Normal consistency results for LC3 compared with CM.

As the graph show, the control mix has the least W/B ratio in comparison with all LC3 paste naturally because with the presence of clay the amount of water will increase more water than CM. Also, there is a clear trend shows that with the increase of clay content the W/B ratio increasing in all the three clay types. Similar result was reported in Nithya Nair study that shows water demand increase with the presence of clay due to high fineness caused by narrow particle size distribution and sheet like structure [1]. Also, with the increase of clay there will be less clinker to clay and lime stone ratio and lead to increasing the amount of water needed in the mix.

4.3.2 Setting time

Setting time paste has the same W/B ratio obtained from normal consistency. The results of the test were both initial and final setting time. The results are as following the figure

24:

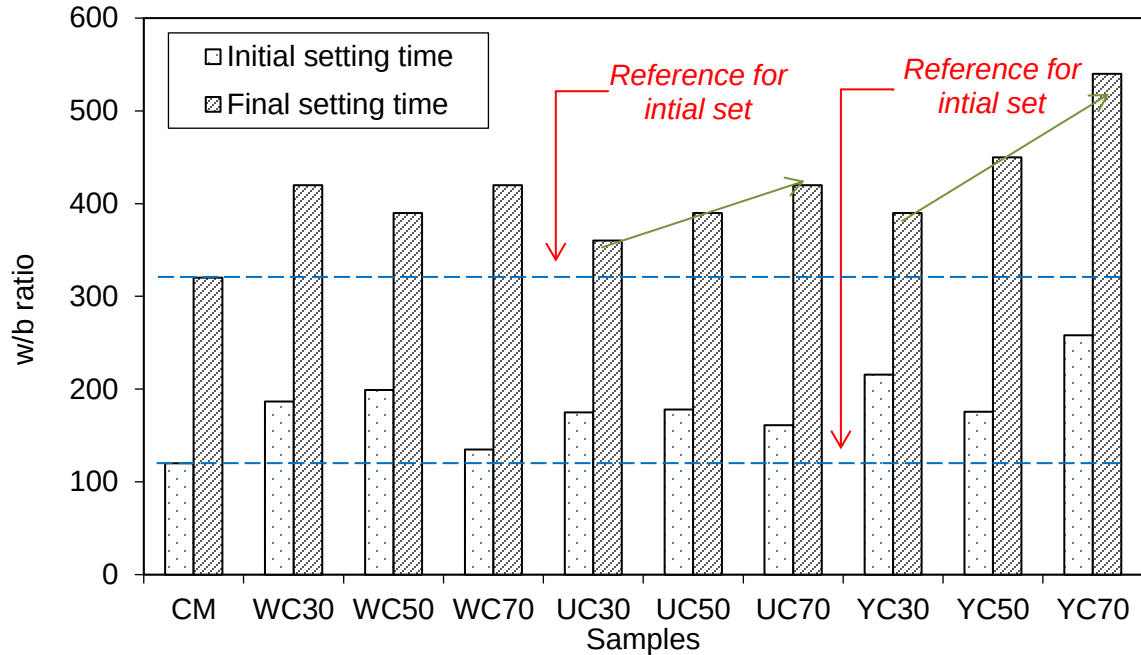


Figure 24 Initial and final setting time result for CM and LC3 mixed.

LC3 reaction can be considered as a pozzolanic reaction which means that part of the reaction will take place after the initial reaction happen from the clinker. The graph also shows that both initial and final setting time of the CM were less than all the LC3 mix with all the replacement. The initial setting time was close between the replacement levels for each mix of LC3. Also, WC and UC have close initial setting time but, YC have a little higher setting time. In final setting time, there is a clear trend that with increase of clay the time needed for final setting time increase. This result was opposite of the result shown in Sreejith Krishnan study and Nithya Nair study were it was reported an early setting time as the more metakaolin the earlier setting time as the induction period reduced with less clinker [1,20]. While in Lei Wang study it's reported that with low clay content the setting time decreased due to the reduction of free water that been absorbed by the clay but, with higher substitution of clinker by LC3 the setting time increase as it traced the pozzolanic

reaction of LC3 [17]. This shows why with 30% replacement the setting time was near to the CM and with increase of clay the setting time increase more.

4.3.3 Flow-table

Flow-table was measuring the percentage of increase in diameter of the sample after the 25 drops of the table. The initial bottom diameter of the sample was 100 mm and after the drops the sample will expand and measured using measuring tape. After that the increase in bottom diameter were calculated. The results of the test are shown in figure 25:

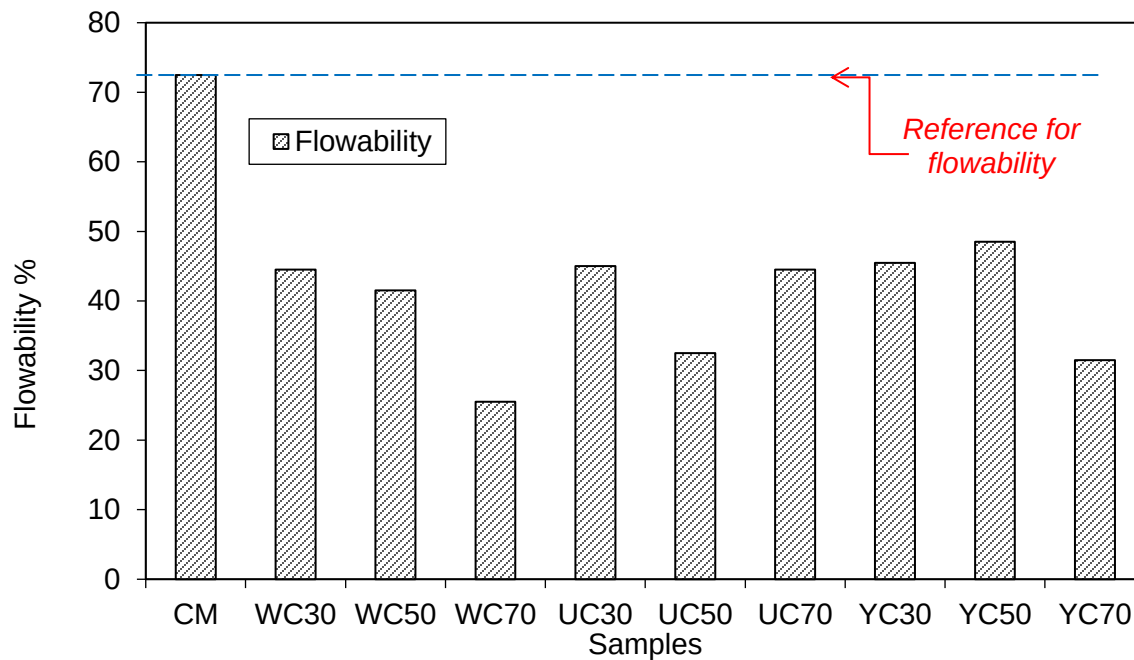


Figure 25 flow-table test results for CM and LC3 mixes.

The results show that the CM has a higher flowability than all LC3 mixes. Generally, with 30% replacement have higher flowability than 50% and 70% replacement respectively because the clinker content is higher and with more clay content the mixes tend to be less flowable. A clear trend is shown with mixes that with increase of clay content the flowability decrease in LC3 as was be proved in Pengkun Hou study [36].

4.3.4 Slump test

Concrete slump test was performed directly after removing the concrete from the mixer.

The slump was measure using measuring tape. The results of slump test were as following

figure 26 and the amount of SP for every mix showed in figure 27:

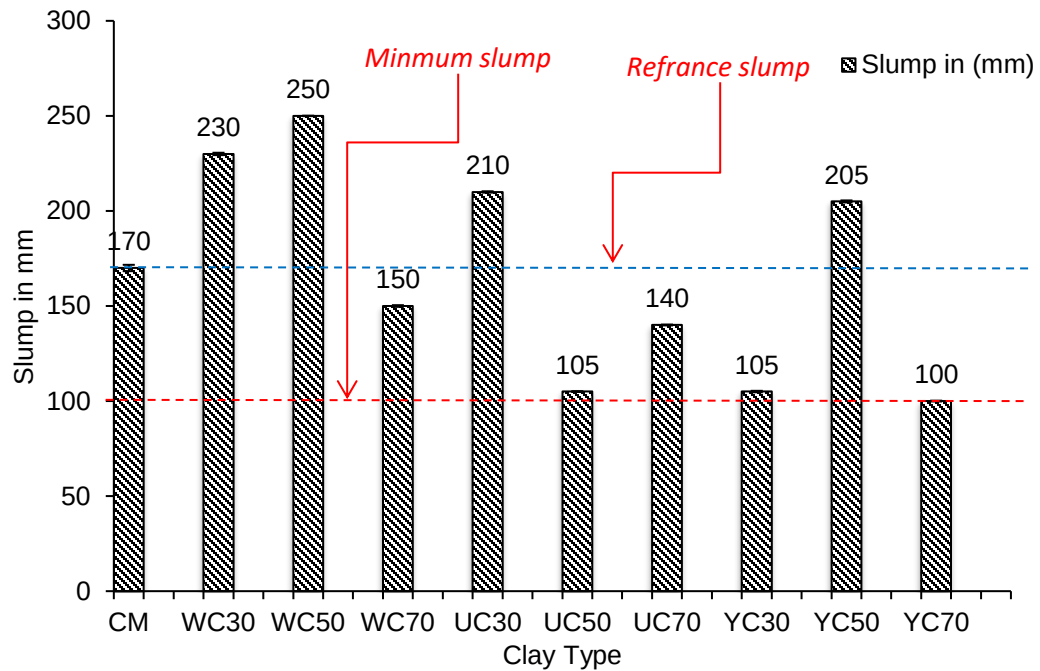


Figure 26 Concrete slump results in mm for CM and LC3.

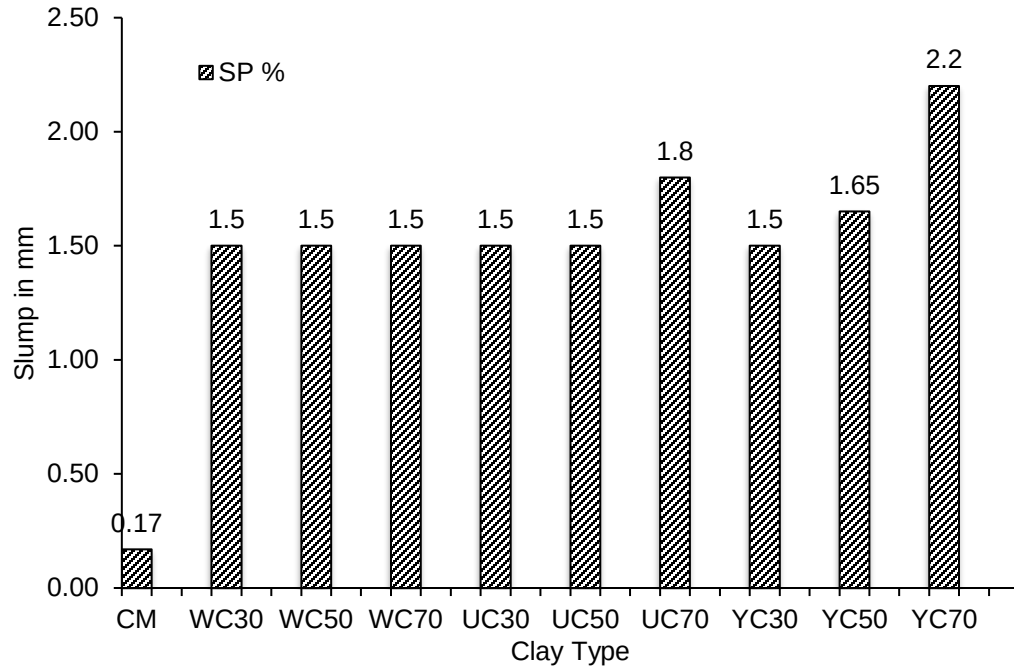


Figure 27 SP content in percentage for CM and LC3 mixes.

The slump was controlled in order to make the minimum slump of 100 mm. The SP was fixed at 1.5% but, with higher clay replacement in UC and YC the SP percentage has increased to 1.8 % and 2.2 % to make them pass the 100 mm slump. The trend of slump is not clear due to different amount of SP % the main goal is to make a good workable concrete. Depending on the percentage of SP the least workability was YC70 then UC70 and YC50. The other mixes can be compared using the chart since all of them have the same SP content. CM had a slump of 80 mm without SP so, a 20 g were only added of SP (0.17%) to enhance the workability in order to pass the minimum slump of 100 mm the result was increase in the slump to 170 mm. The need of SP in order to get good workability LC3 concrete have been shown in Nithya Nair study as with 0.3 W/B ratio the targeted slump was not achieved even with high SP content and the W/B ratio was increased to 0.4 with addition of SP to get targeted slump [1]. The slump measuring is shown in figure 28 and 29.



Figure 28: Slump test measuring for UC 70.



Figure 29 Slump test measuring for YC 50.

From these results of the three fresh properties experiments performed in the LC3 paste, the effect of clay in the paste clearly of increasing the W/B ratio as it's natural for clay to have a high-water absorption, this increase in water will increase the setting time for the LC3 as it's been shown with the YC by having the highest W/B ratio and have the highest setting time alongside with the nature of pozzolanic reaction. The other two types of clay WC and UC have similar trend on the three replacement levels. Although the W/B ratio increase in LC3 and its effect on increasing the setting time was clear, the flowability which is mainly increasing with the increase of W/B ratio have decreased in case of LC3 paste.

The CM was having the highest flowability in comparison with LC3 and with increasing of the clays the flowability decrease (even with higher clay W/B ratio in higher clay replacement). Similar behavior can be notice with concrete fresh slump test. CM mix has the lowest SP content of 0.17 to reach 170 mm slump. LC3 mixes have SP of 1.5 to pass 100 mm slump and some LC3 needed higher SP content than 1.5, these results show that LC3 have less workability than CM in both paste and concrete using flow-table and slump test respectively.

4.4 Mechanical properties results

4.4.1 Compressive strength concrete

Compressive strength was measure in concrete cylinder and cubes, mortar cubes and paste cubes. These tests were focusing on comparing the LC3 mixes with CM to see how the strength will be affected. Concrete cylindrical samples were tested in 7, 28 and 90 days the results are shown in figure 30:

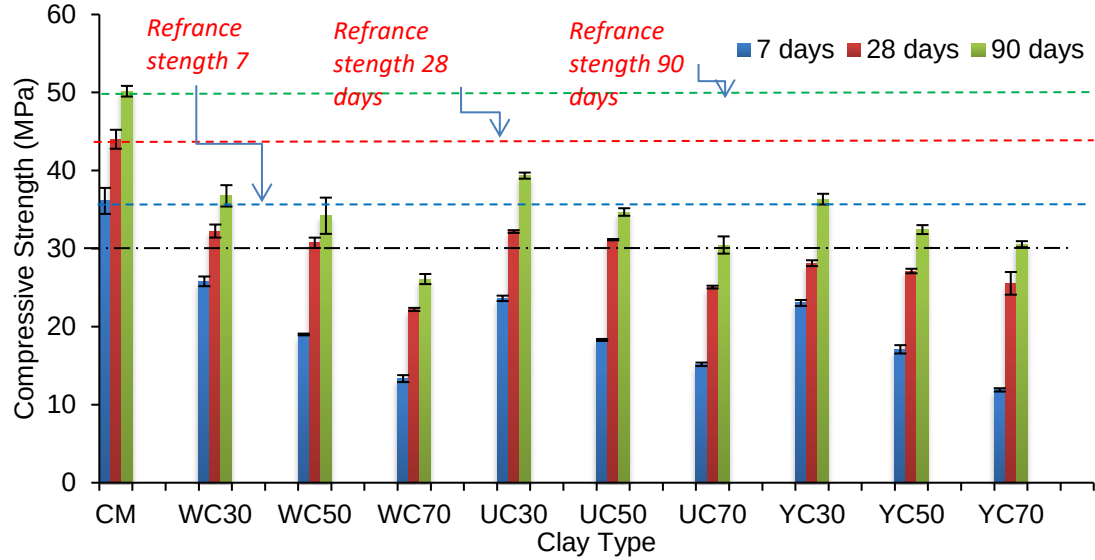


Figure 30 concrete cylindrical compressive strength at 7, 28 and 90 days.

The figure shows that with increase of time the compressive strength increases for all LC3 sample and CM. Also, with increasing the amount of clay, the strength has decreased in all LC3 clay types this decrease in compressive strength is related to the increase of the macro-pores form by the clay and limestone also the low amount of hydration in LC3 with low clinker content [17]. Regardless the substitution rates studied all mix (except WC70) has passed 30 MPa strength in the 90 days but, none have passed 30 MPa in 7 days. In 28 days, WC30, WC50, UC30 and UC50 have passed 30 MPa. The CM was the highest mix in compressive strength in all time intervals with clear gab between LC3 mixes and CM duo to the low amount of kaolinite presence in the clays used.

Concrete cube samples were tested in 28 and 90 days. LC3 and CM cubic samples were having the same behavior as in cylindrical samples both time and replacement. In cubic samples, the difference between the CM and LC3 is less in comparison with cylindrical samples. It does also can be noticed that WC50 and UC30 were having the same compressive strength as CM in 28 days other samples were less than CM in 28 days. In 90

days, CM were having the highest strength and LC3 sample were having a low increase in strength between 28 and 90 days in case of cubic samples. Similar result have been shown in other studies of comparable to (slightly lower) compressive strength in comparison between CM and LC3 [20,37,38] as cube concrete samples were used in these studies. These results are shown in figure 31:

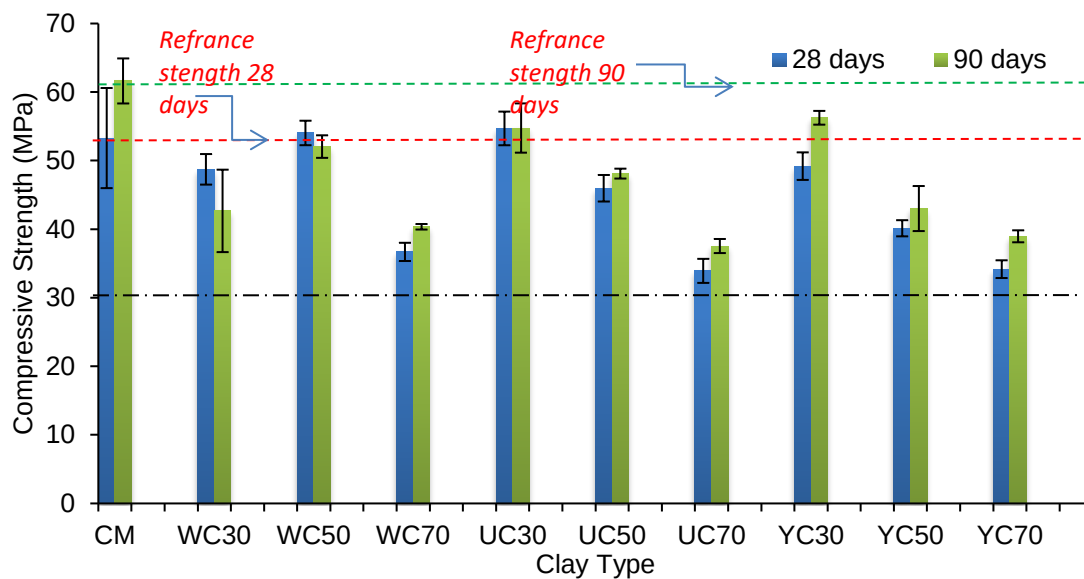


Figure 31 Concrete cubic compressive strength at 28 and 90 days.



Figure 32 concrete cubic compressive strength cubes after the test



Figure 33 concrete cubic compressive strength cubes after the test

4.4.2 Compressive strength mortar

Mortar compressive strength samples were tested in 7 and 28 days. In LC3 mortar, the compressive strength is low in 7 days strength. In the 28 days, the increase in strength can be notice compared with the 7 days strength. Higher substitution rate showed decrease in compressive strength. Some previous study show an increase in compressive strength at 28 days as they use high purity metakaolin while in Quang Dieu Nguyen study a low grade metakaolin were used LC3 mortar had lower compressive strength as the substitution increased [39] . The results of mortar compressive strength are shown in figure 34:

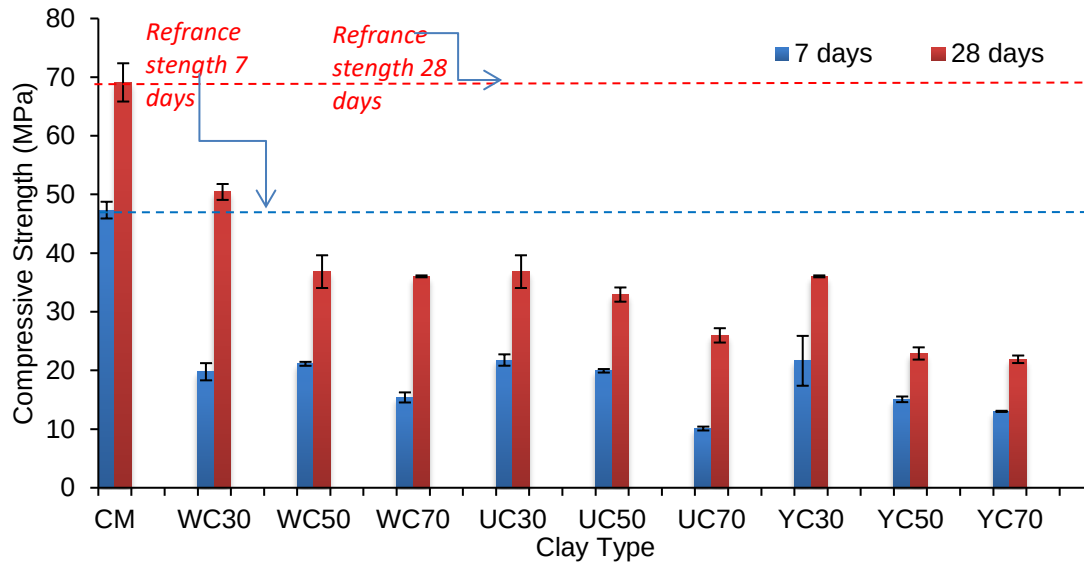


Figure 34 mortar cubic compressive strength at 7 and 28 days.

4.4.3 Compressive strength paste

Paste samples were tested in compressive strength at 7, 28 and 90 days. All paste samples (except YC70) have passed 30 MPa at 28 days. The compressive strength has increased with time and decrease the strength with higher clay replacement. CM mix were having the same strength or lower in comparison with (WC30/50/70, UC30/50 and YC30/50) at 7 days but, in 28 days CM were having the highest compressive strength comparing with all LC3 mixes. The result of compressive strength of LC3 paste is shown in figure 35:

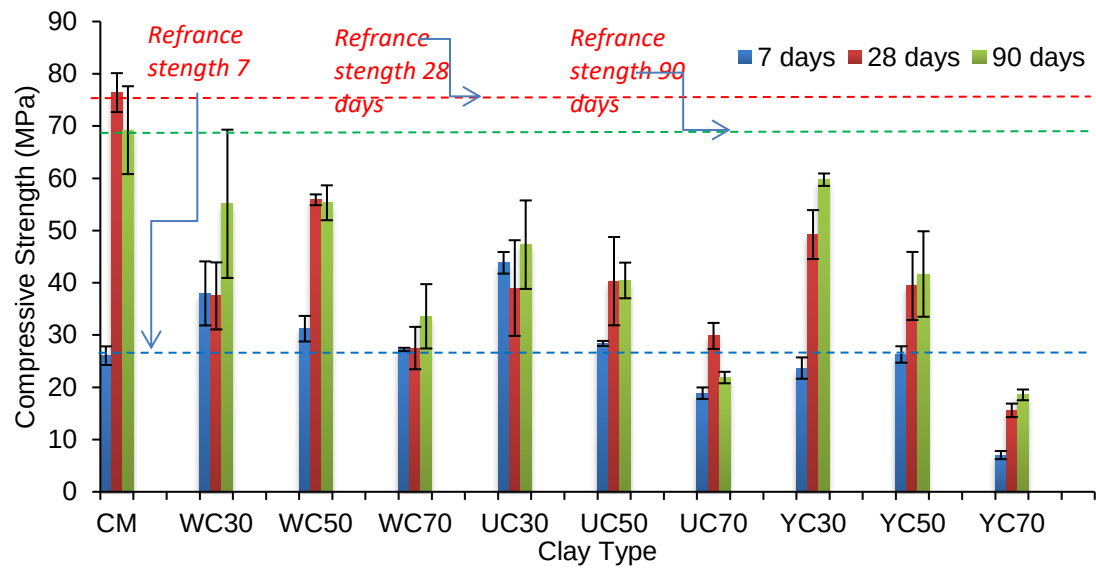


Figure 35 paste cubic compressive strength at 7,28 and 90 days.

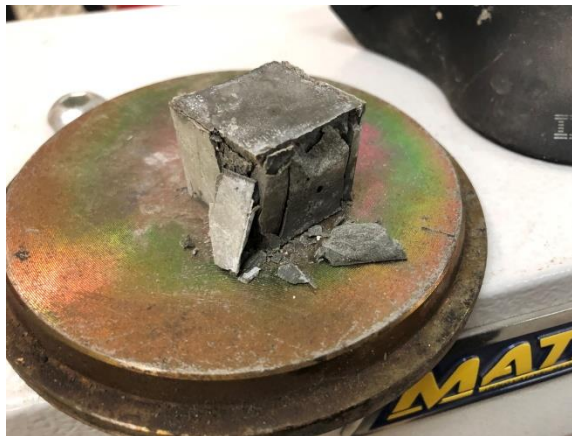


Figure 36 paste cubic compressive strength after the test



Figure 37 paste cubic compressive strength after the test

From these result of compressive strength at different time intervals for concrete mortar and paste all mix have passed 30 MPa compressive strength which make the LC3 can be considered as structural concrete. CM was having the highest compressive strength in comparison with LC3 at 28 and 90 days as low-grade kaolinite clay were used [39]. All mixes were having the same behavior of increasing the strength with time and decreasing with higher clay content duo to the increase of the macro-pores and low amount of hydration in LC3[17].

4.4.4 Modulus of elasticity

Modulus of elasticity was tested with the cylindrical concrete mixes. The setup of 2 rings with 2 LVDTs was shown in figure 10. The modulus of elasticity was tested in 7, 28 and 90 days. The results of 7 days were shown in figure 38-40:

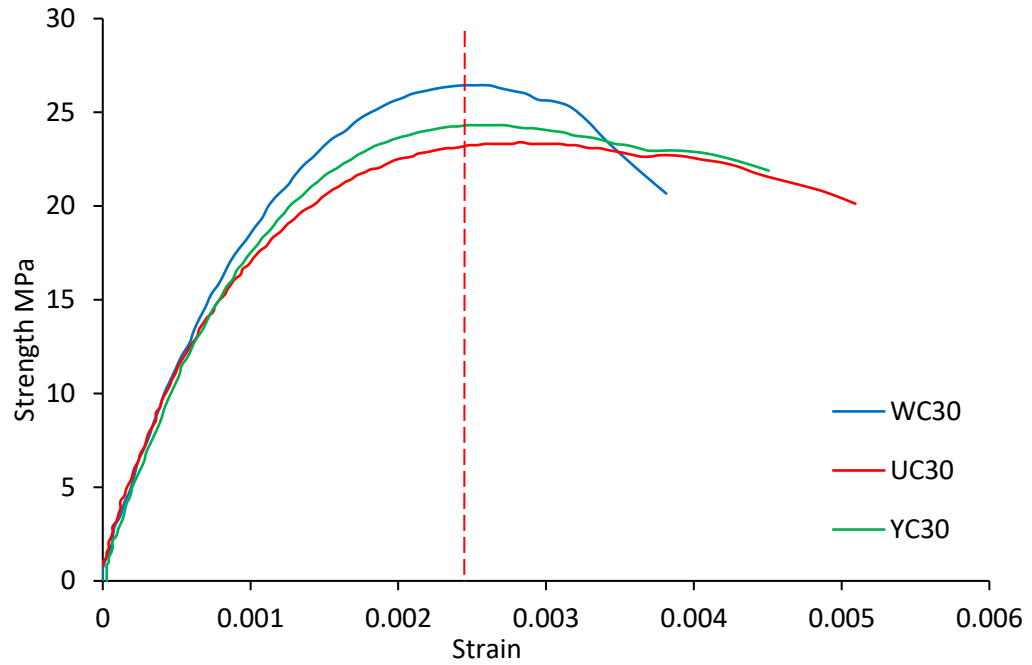


Figure 38 Modulus of elasticity for WC, UC and YC with 30% replacement at 7 days.

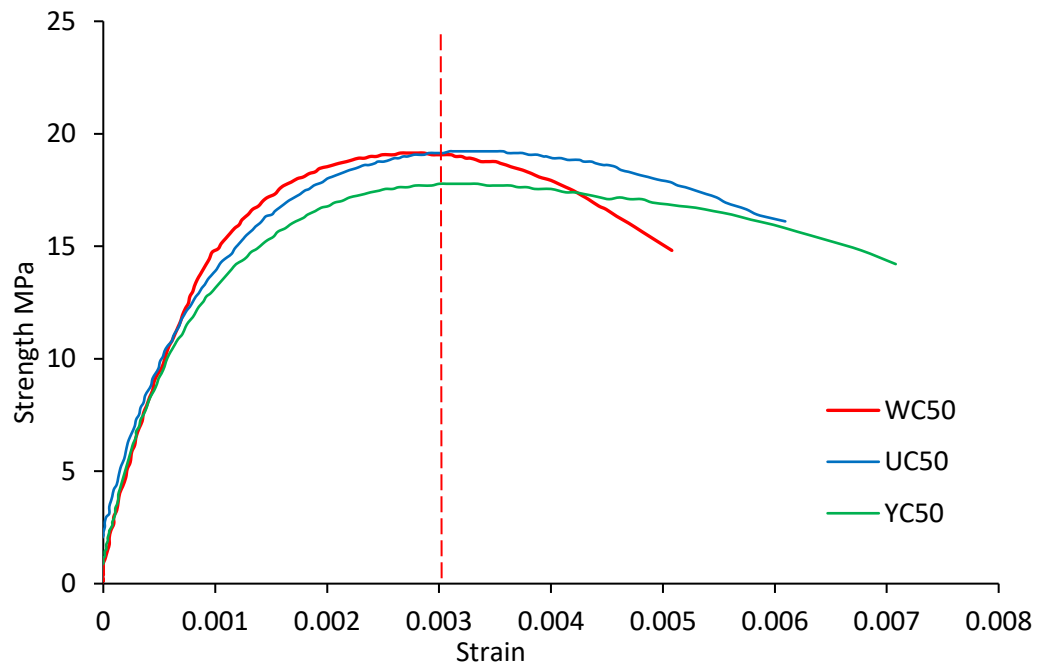


Figure 39 Modulus of elasticity for WC, UC and YC with 50% replacement at 7 days

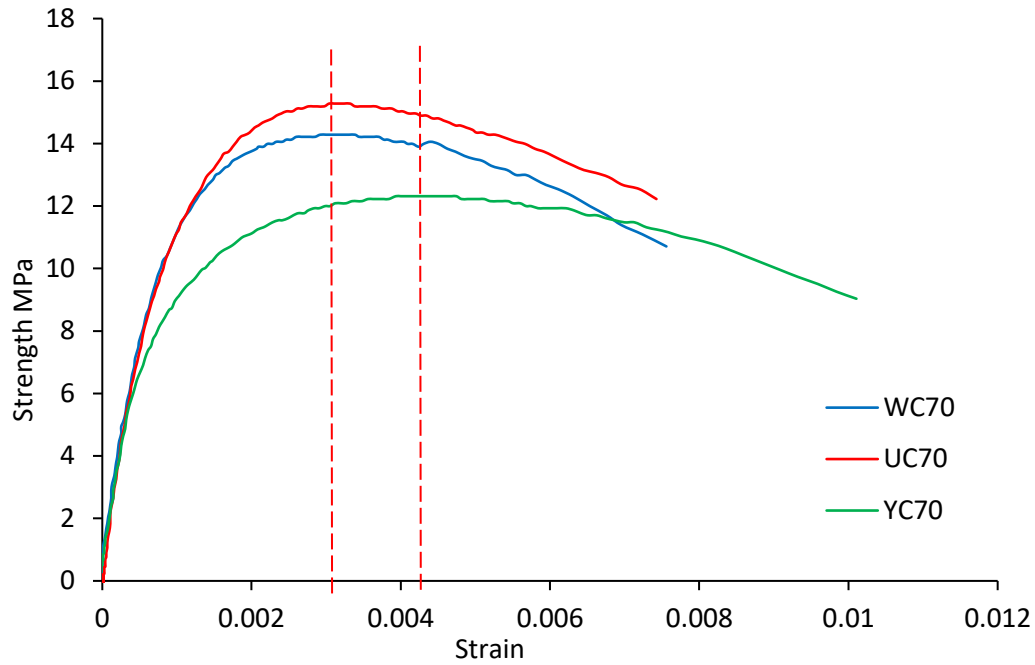


Figure 40 Modulus of elasticity for WC, UC and YC with 70% replacement at 7 days

The results of the 28 days were shown in figure 41-43:

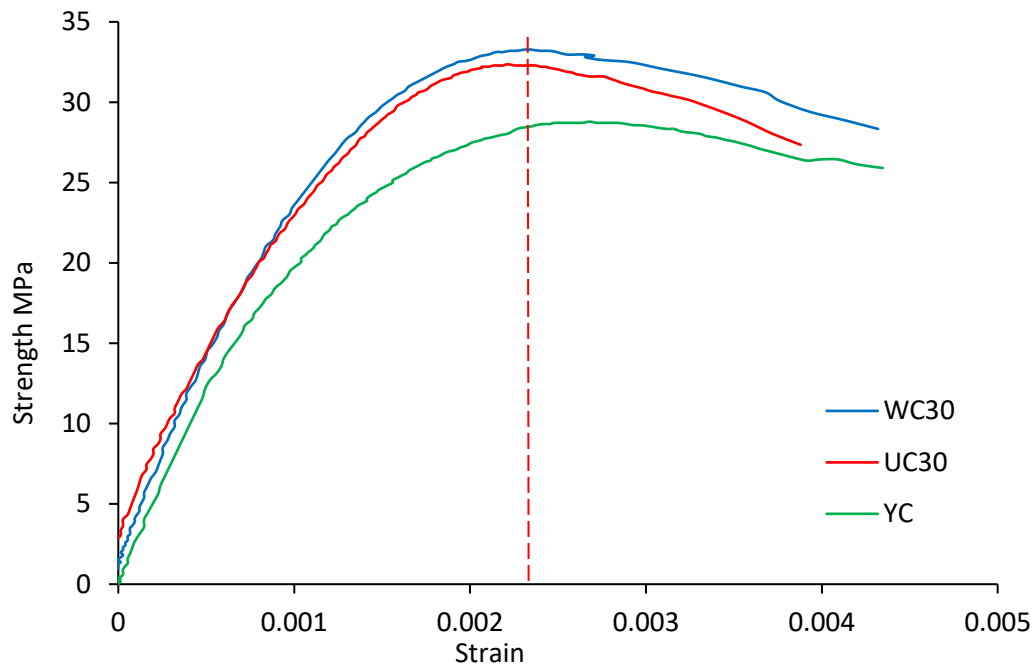


Figure 41 Modulus of elasticity for WC, UC and YC with 30% replacement at 28 days

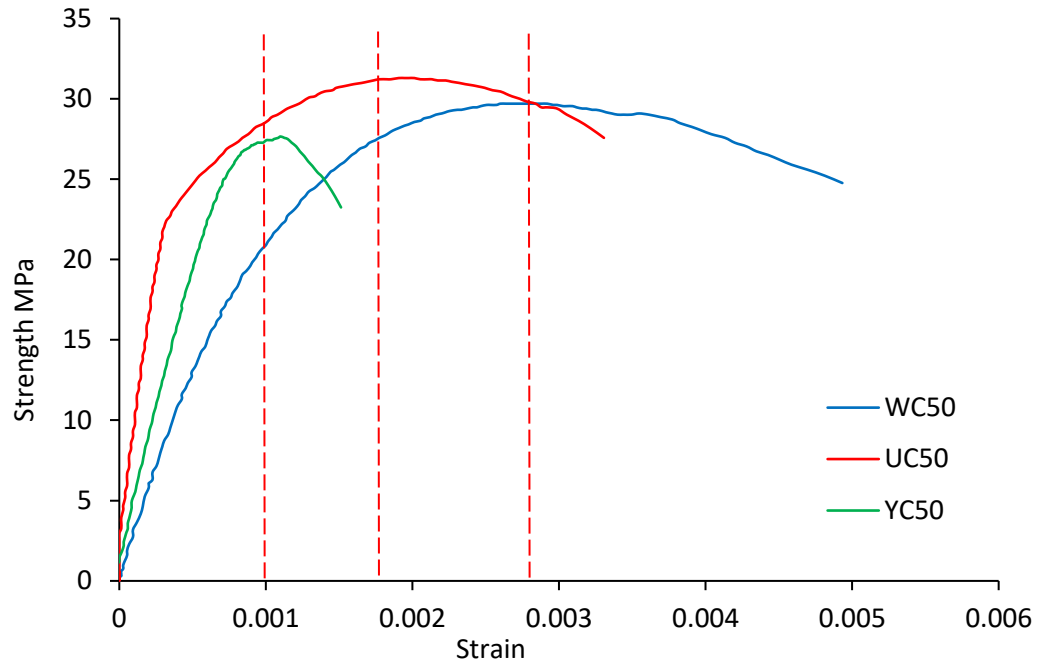


Figure 42 Modulus of elasticity for WC, UC and YC with 50% replacement at 28 days

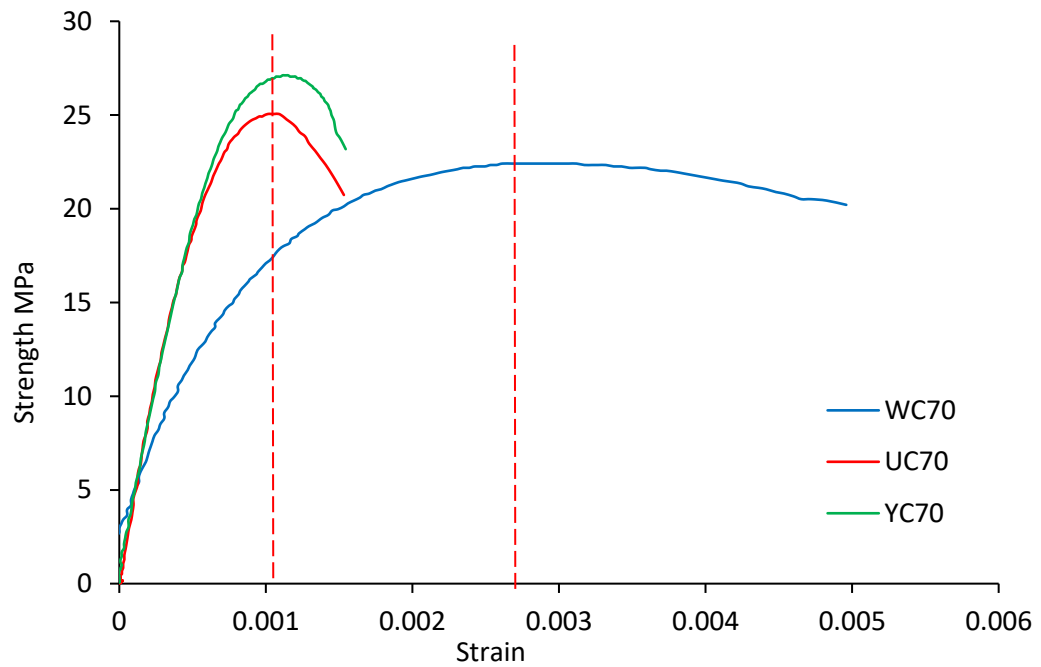


Figure 43 Modulus of elasticity for WC, UC and YC with 70% replacement at 28 days

The results of the 90 days were shown in figure 44-46:

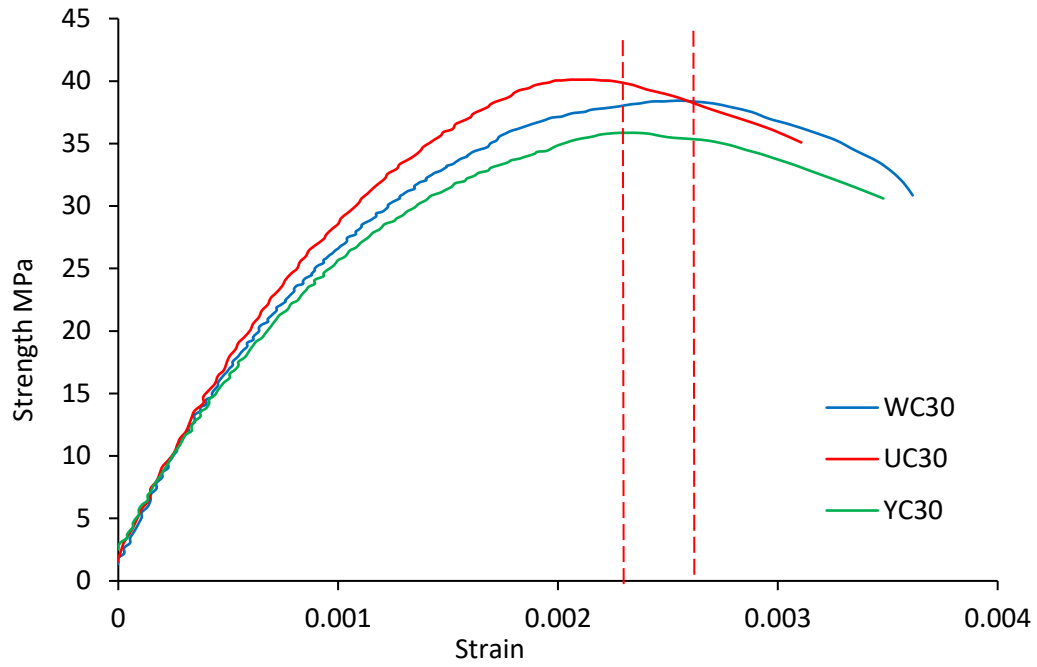


Figure 44 Modulus of elasticity for WC, UC and YC with 30% replacement at 90 days

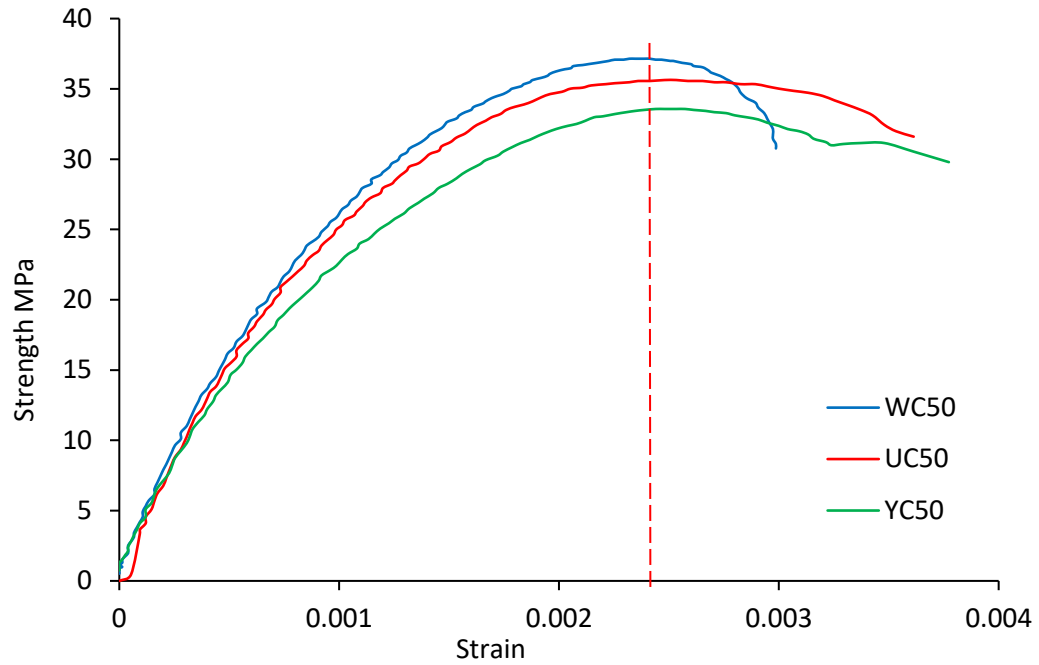


Figure 45 Modulus of elasticity for WC, UC and YC with 50% replacement at 90 days

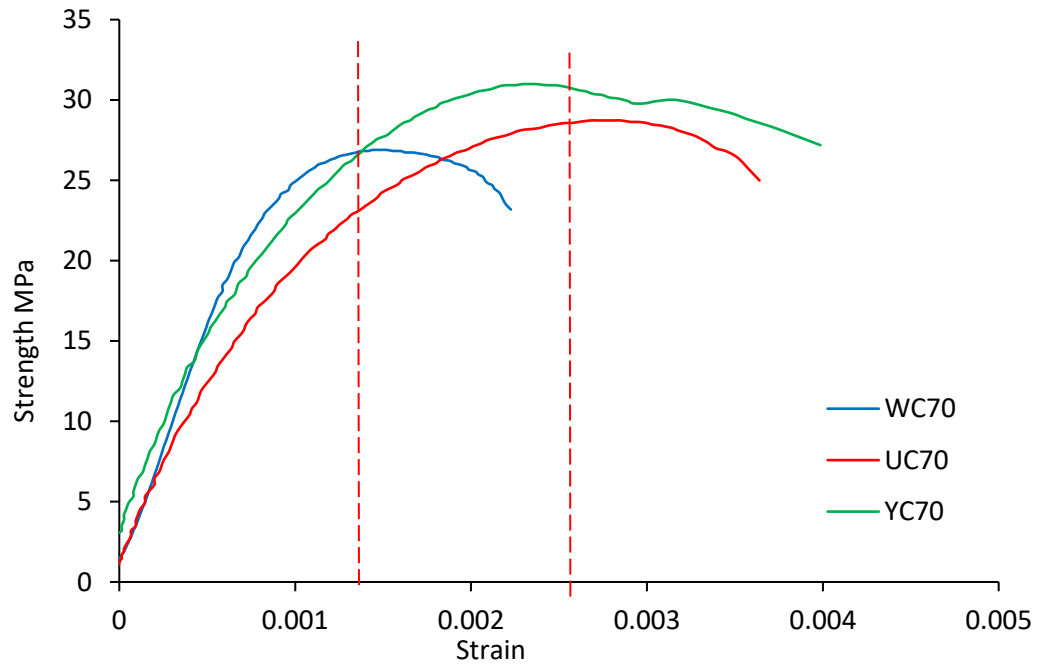


Figure 46 Modulus of elasticity for WC, UC and YC with 70% replacement at 90 days

Almost all samples were having a 0.003 strain or less for all testing time and clay replacement. These results can be compared with CM in the following figure 47:

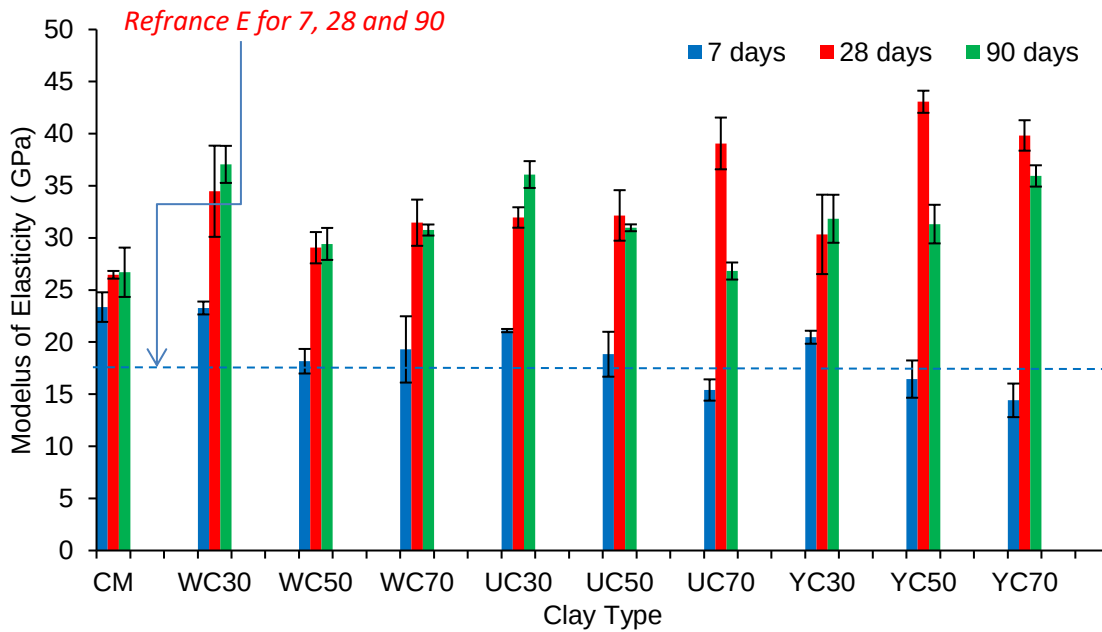


Figure 47 modulus of elasticity for LC30 compared with CM.

As it can be seen in the figure, at 7 days CM were having higher modulus of elasticity than LC3 mixes but, at 28 and 90 day the modulus of elasticity of LC3 have increased to be higher than CM which gain no increase in modulus of elasticity with time. Studies show that LC3 have comparable to little higher modulus of elasticity compared with CM around 40 GPa [35,37,40]. These result shows that the LC3 is stiffer than CM as it has a higher modulus of elasticity.

4.4.5 Shrinkage

Shrinkage of LC3 was measured in 100 days after a curing period of 28 day curing under water. The entire shrinkage samples were having a W/B ratio of 0.4 to compare between LC3 and CM. the result are shown in figure 48:

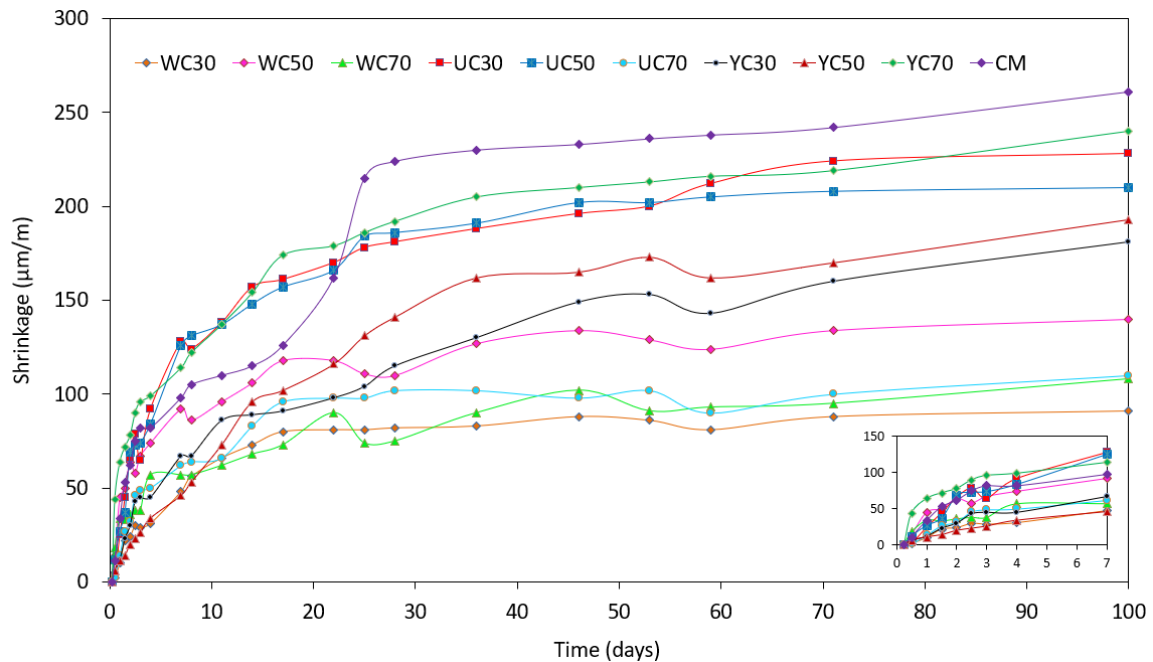


Figure 48 Shrinkage of LC3 and CM for 100 days.

Shrinkage graph shows that CM was having the highest shrinkage compared to all LC3 mixes. The graph shows that WC with average of the three replacements was having the lowest reading. In UC the 30% and 50% replacement were having similar shrinkage and UC70 have lower than UC30 and UC 50. The graph shows a clear trend with YC30, it had the lowest shrinkage compared with YC50 then YC70 respectively. Yuvaraj Dhandapani studied the development in autogenous and total shrinkage for prismatic and cylindrical samples within period of 400 days shows that at early age (less than 100 days) there was no significant difference between LC3 and CM [10]. It's also have been reported with metakaolin substitution of 5% to 15% have lowered both autogenous and drying shrinkage while limestone with substitution of more than 20% have increase the drying shrinkage and combined in LC3 concrete the total shrinkage have similar to higher shrinkage at later age [10].

4.5 Micro structure and characterization of hydrated samples

In order to have a good understanding of our materials micro-structure analysis is needed to get clear idea about the chemical reaction and the final result of the reaction of the LC3 mixes XRD, TGA and SEM/EDS were obtained on LC3 paste to study its micro structure properties.

4.5.1 XRD

XRD were tested on powder sample passed sieve #200 these sample were taken from pasted sample after 28 days. The results of XRD are shown in figure 49-51:

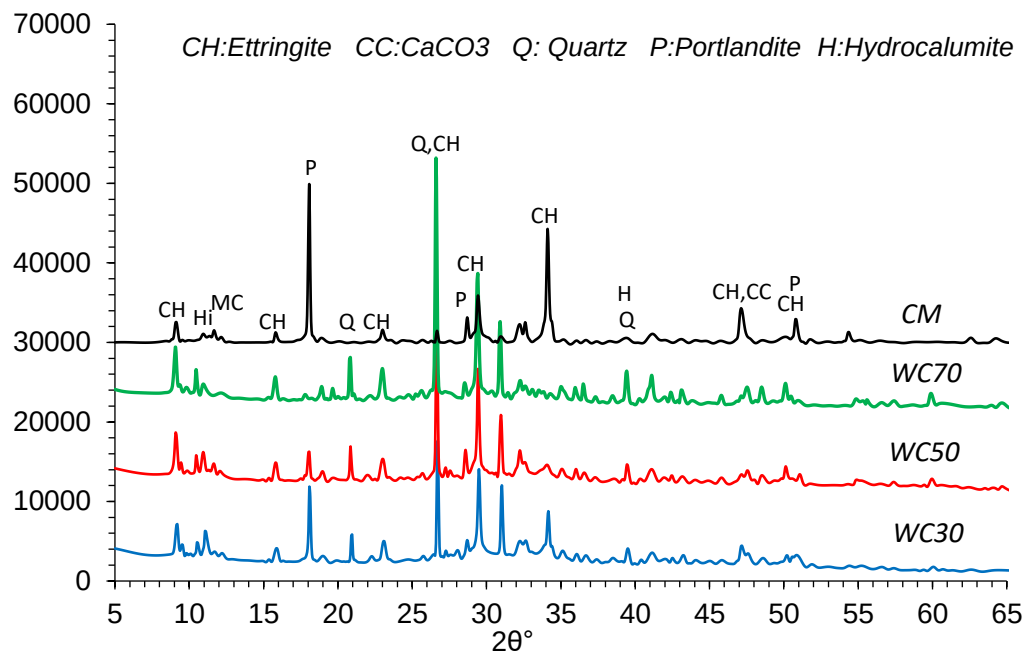


Figure 49 XRD for WC paste powdered samples after 28 days

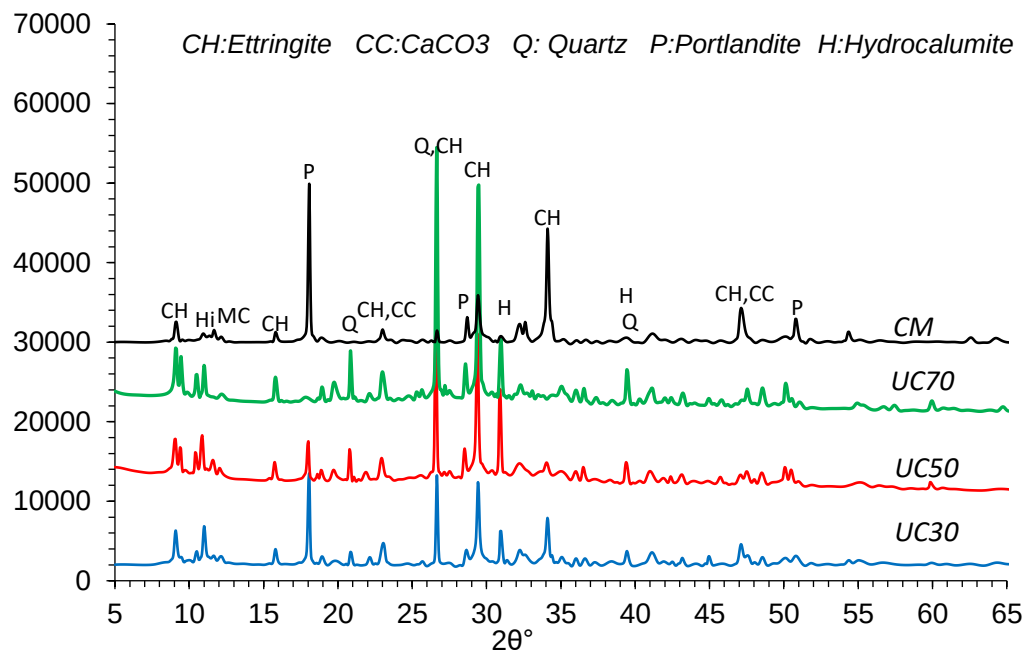


Figure 50 XRD for UC paste powdered samples after 28 days

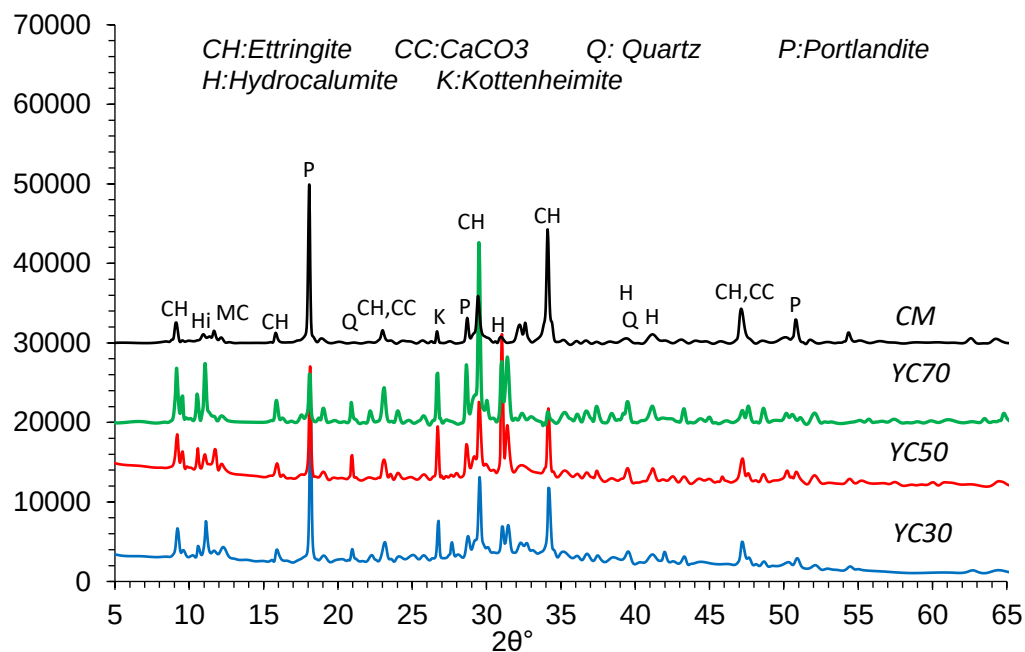


Figure 51 XRD for YC paste powdered samples after 28 days

XRD results show that the main components are ettringite, portlandite, calcium carbonate and hydrocalumite. Other materials are available in smaller amounts and form only very

small peaks. The portlandite peak at 18.3 degree is highest in CM mix and it's lower with the increase of clay for all clay types. Also, the ettringite is noticed to have a higher value in CM in degrees of 47.5 and 34 but, at 9 and 29.5 degrees ettringite is higher in the clays than the CM and with increase of clay content. Other studies have showed the formation of ettringite at the same angles of 9, 16 and 23 [3,41,42]. Hydrocalumite is forming only in clays and with high amount in higher clay replacement and only form a small hump on CM mix. The lower the clay replacement the higher monocarboaluminate formed and with higher clay replacement the higher Hemicarboaluminate formed [3].

4.5.2 TGA

TGA were tested on powder sample passed sieve #200 these sample were taken from pasted sample after 28 days. The results of TGA are shown in figure 52-54:

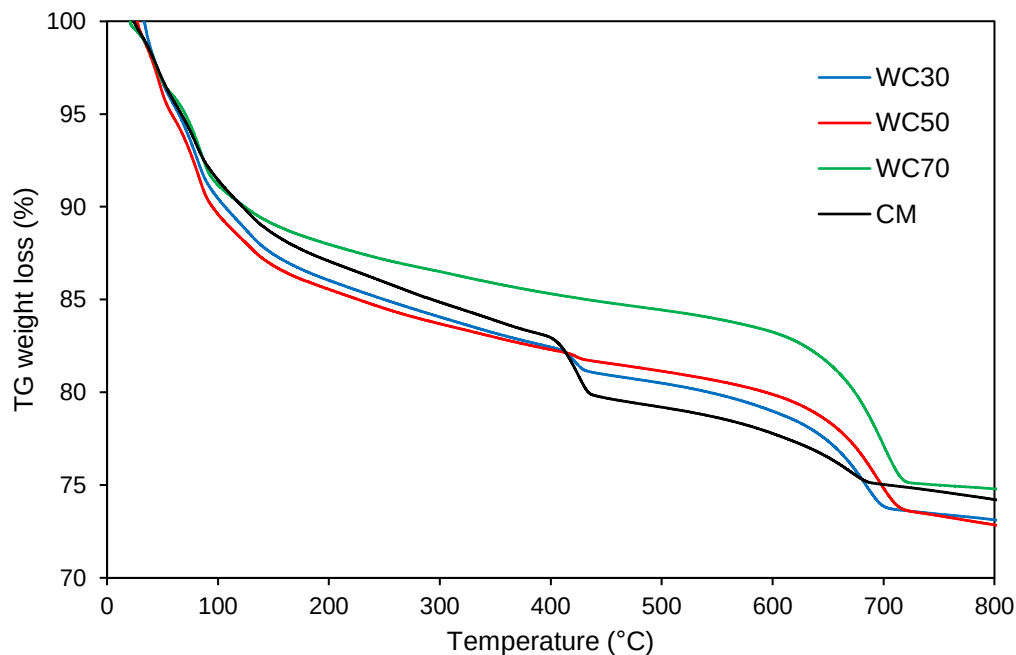


Figure 52 TGA analysis for 30% replacement Paste powdered samples after 28 days.

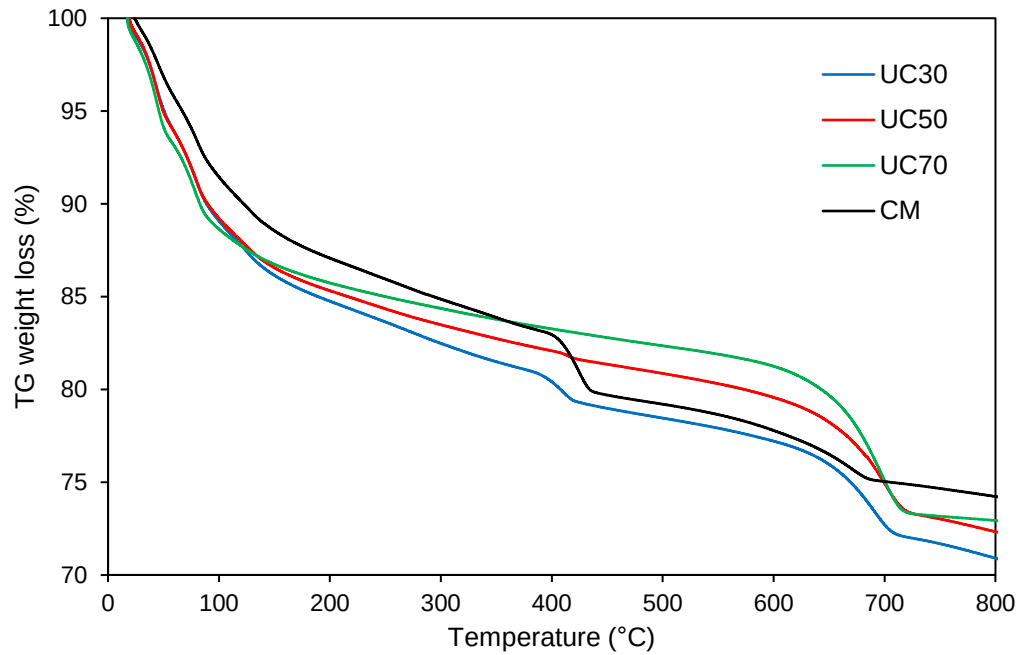


Figure 53 TGA analysis for 50% replacement Paste powdered samples after 28 days

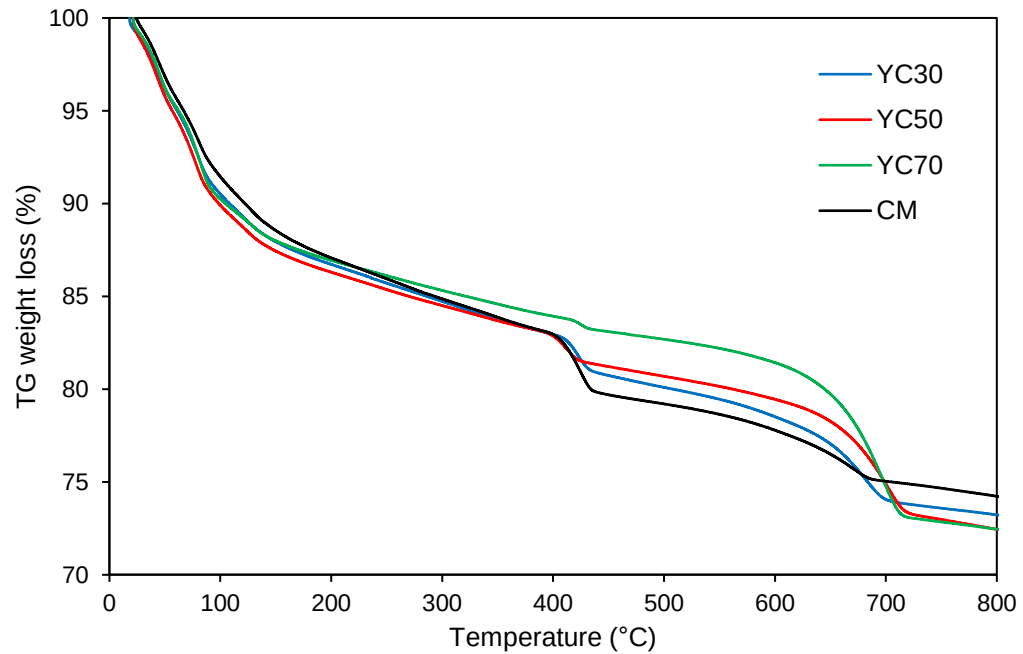


Figure 54 TGA analysis for 70% replacement Paste powdered samples after 28 days

TGA results show that all the clays have the same reduction in weight from 20% to 25 %.

TGA pattern of reduction in weight is similar in all clay types and it's comparable with

CM. the reduction in weight can be divided into 3 main regions: first between 0 to 150 °C which caused by the dehydration of monocarbonates, calcium silicate (C-S-H) and Aft, Aftm phases. Second between 400 to 450°C caused by the dehydration of portlandite. Thirdly between 650 to 750 °C caused by the de-carbonation of calcite (CaCO_3) [18,35,41].

4.5.3 SEM/EDS

From the same samples the have been tested in XRD and TGA a small pieces of paste sample were taken to do SEM/DES test to check the results of XRD and to have more accurate results for our samples. The results of SEM/EDS image for WC mixes are shown in figure 55-60:

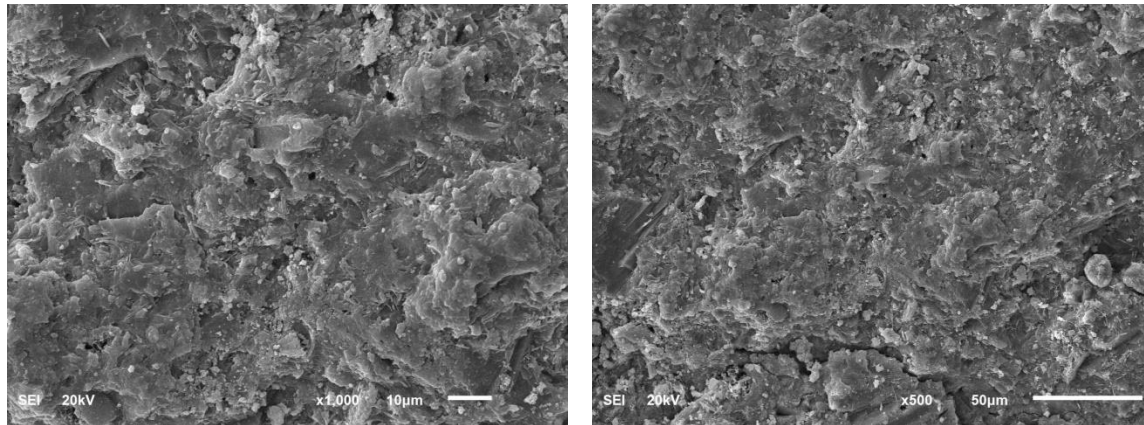


Figure 55 Micro image for WC30 with 10µm and 50µm magnification.

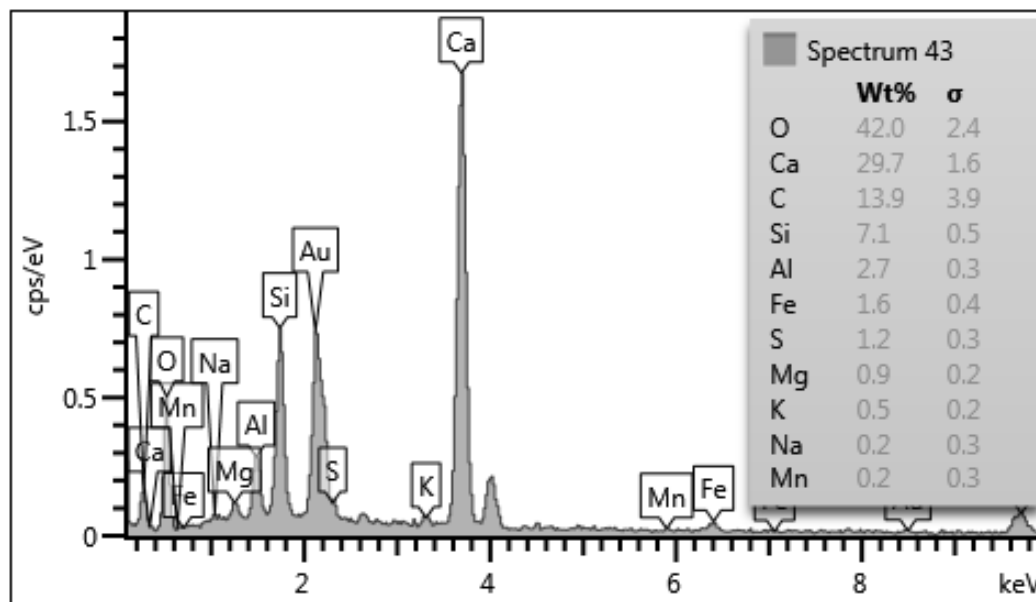


Figure 56 Spectrum analysis for WC30

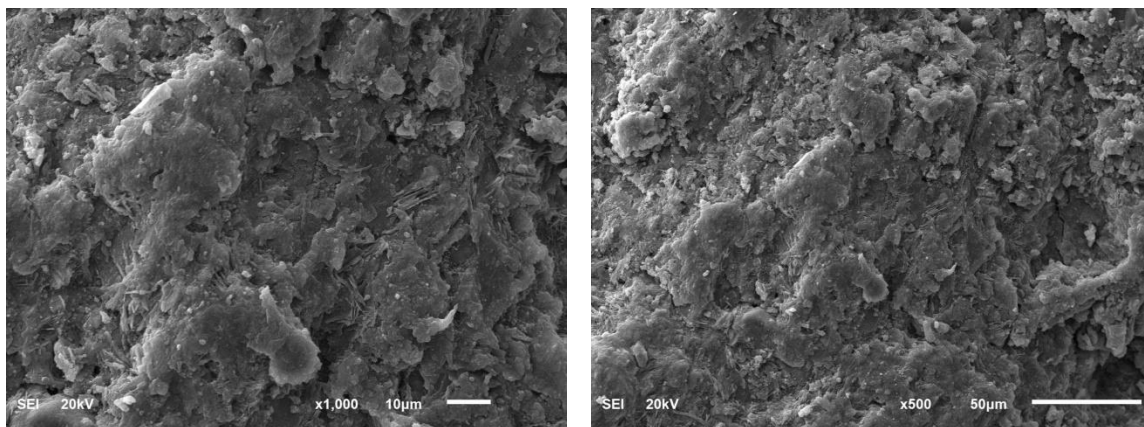


Figure 57 Micro image for WC50 with 10μm and 50μm magnification

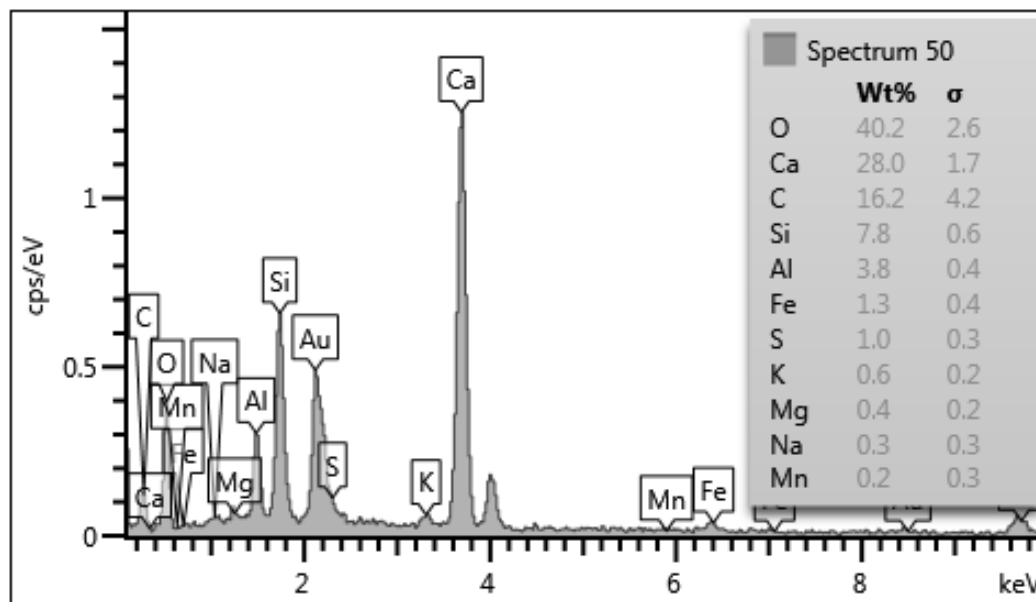


Figure 58 Spectrum analysis for WC50.

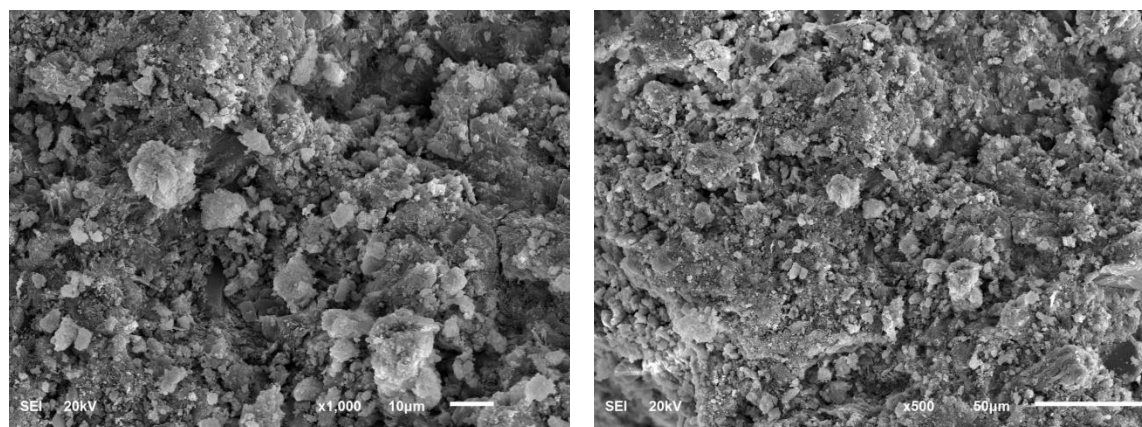


Figure 59 Micro image for WC70 with 10μm and 50μm magnification

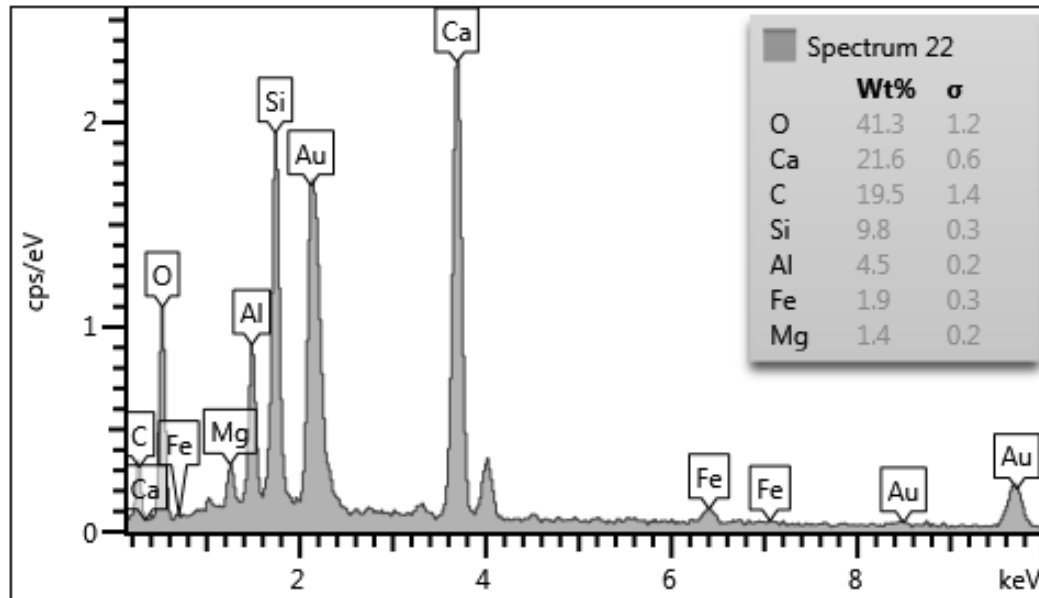


Figure 60 Spectrum analysis for WC70.

Spectrum analysis show that the WC mainly contain of Ca, O, C, Si and Al. these results are matching the result obtained from XRF were the Si and Al are mainly coming from the clay and Ca were coming from the clinker. Increase in the clay the amount result in the increasing of Al and Si and decreasing the amount of Ca while O stays constant.

The results of SEM/EDS image for UC mixes are shown in figure 61-66:

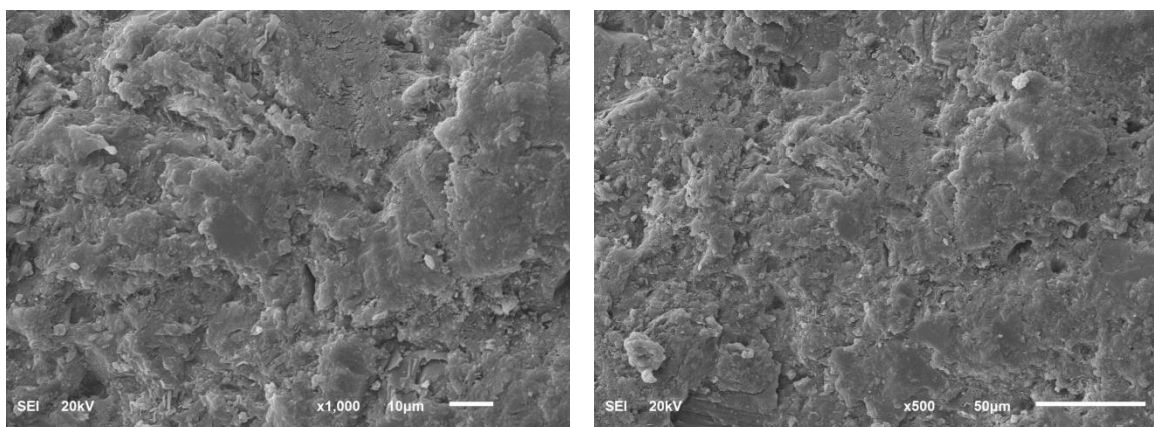


Figure 61 Micro image for UC30 with 10μm and 50μm magnification

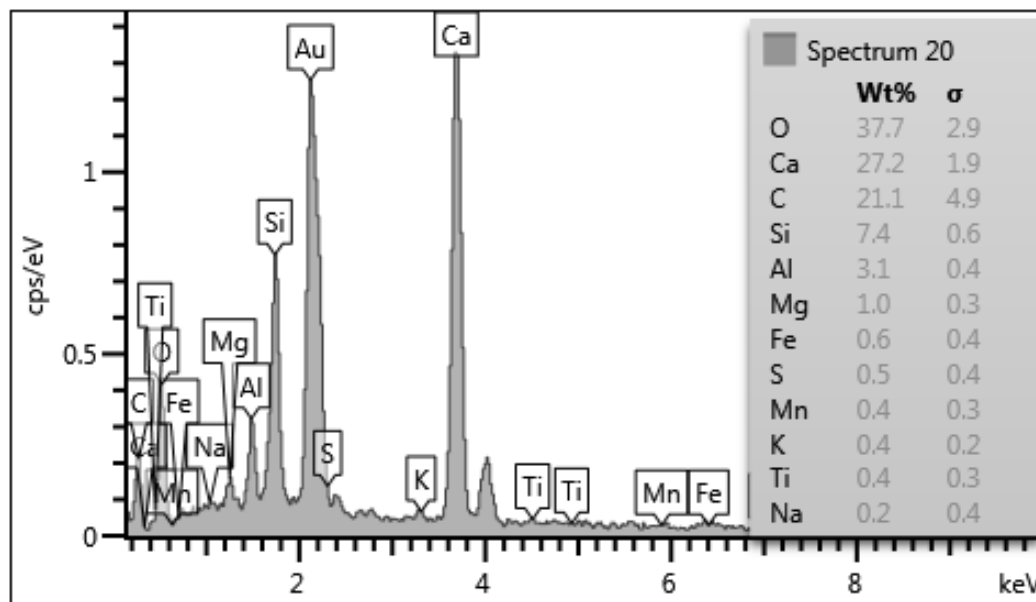


Figure 62 Spectrum analysis for UC30

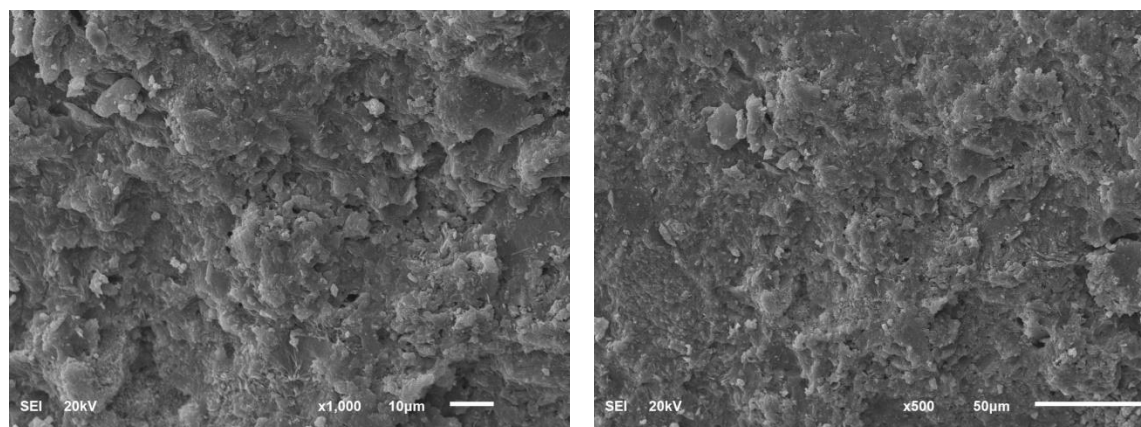


Figure 63 Micro image for UC50 with 10μm and 50μm magnification

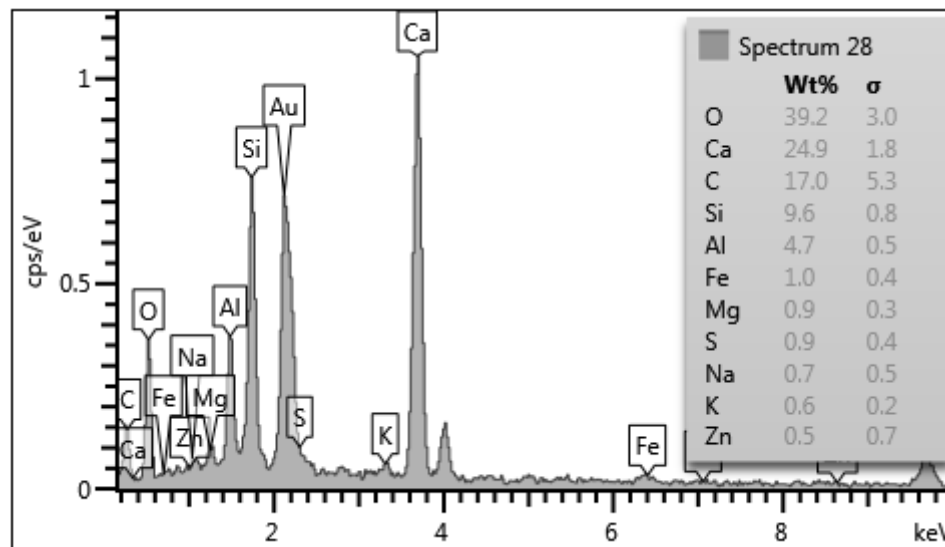


Figure 64 Spectrum analysis for UC50

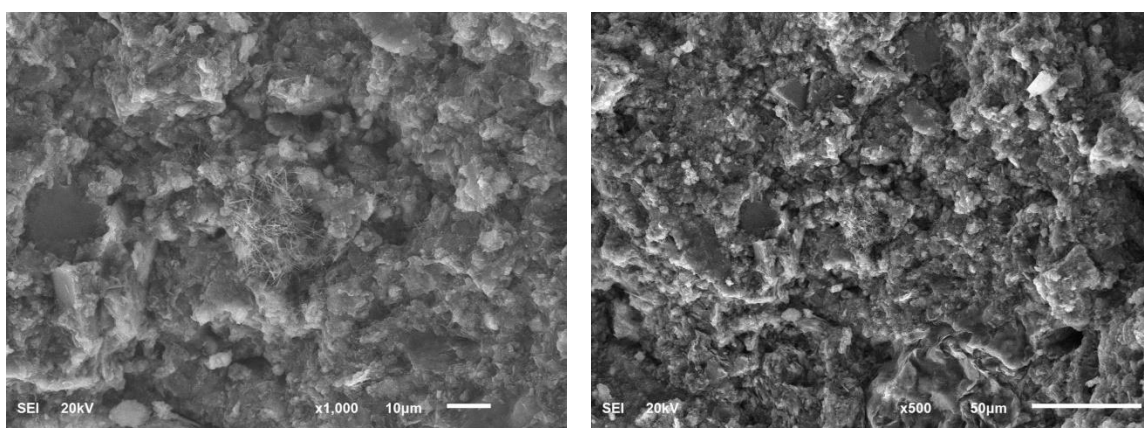


Figure 65 Micro image for UC70 with 10μm and 50μm magnification

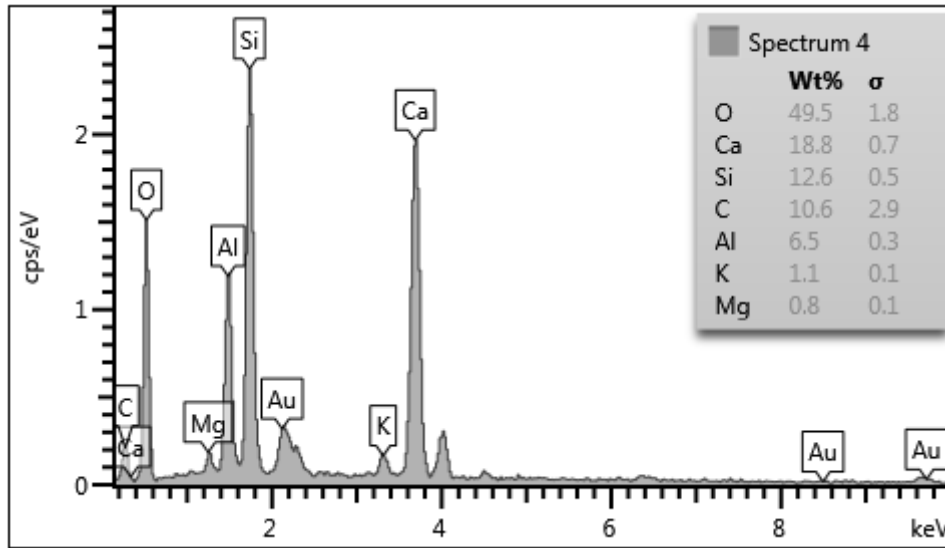


Figure 66 Spectrum analysis for UC70

Spectrum analysis show that the UC mainly contain of Ca, O, C, Si and Al. these result are matching the result obtained from XRF were the Si and Al are mainly coming from the clay and Ca were coming from the clinker. Increase in the clay the amount result in the increasing of Al and Si and decreasing the amount of Ca and C decrease.

The results of SEM/EDS image for YC mixes are shown in figure 66-72:

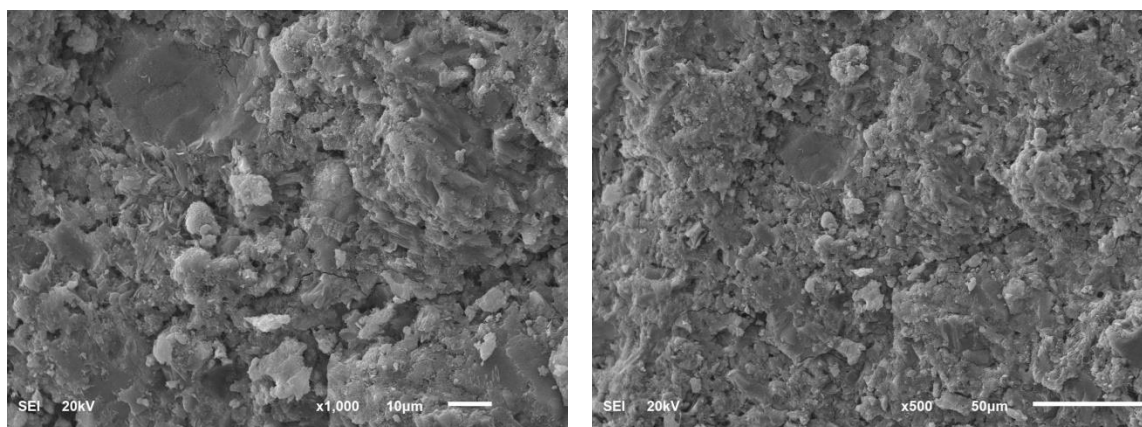


Figure 67 Micro image for YC30 with 10μm and 50μm magnification

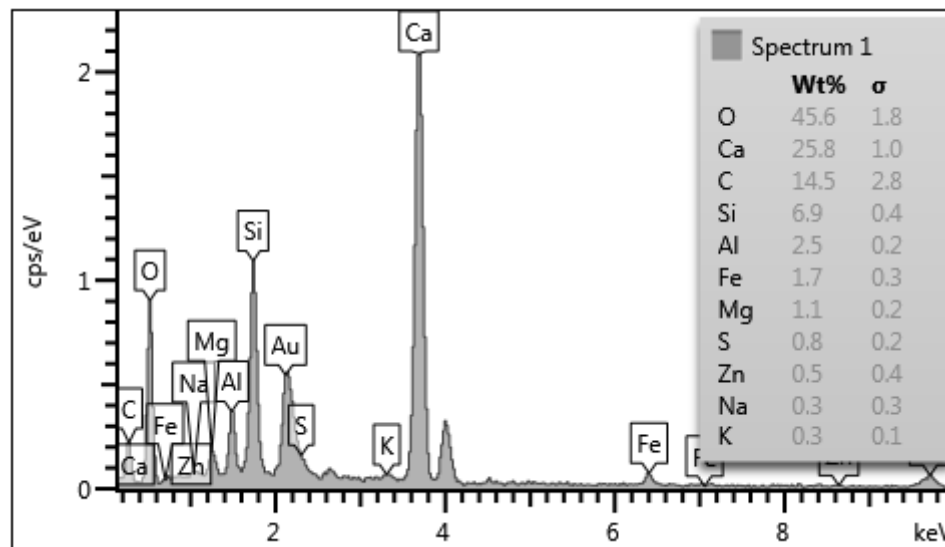


Figure 68 Spectrum analysis for YC30

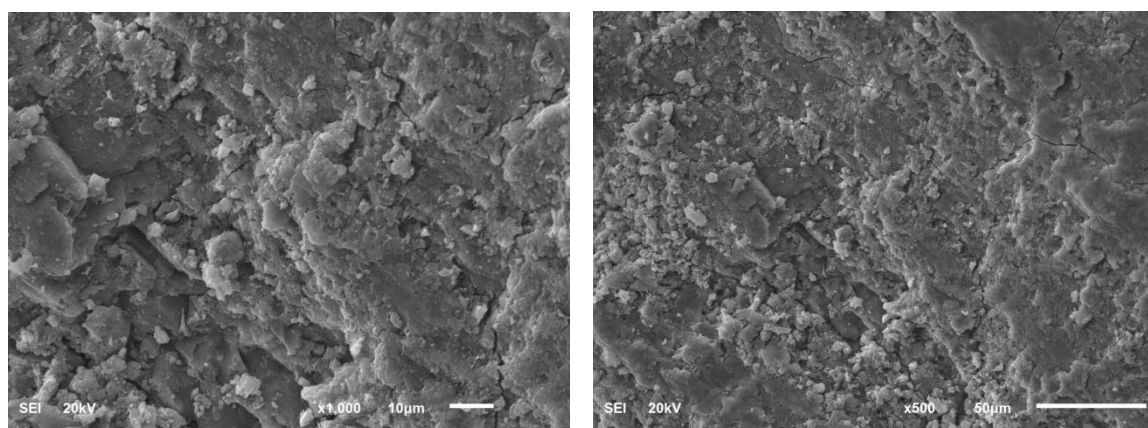


Figure 69 Micro image for YC50 with 10μm and 50μm magnification

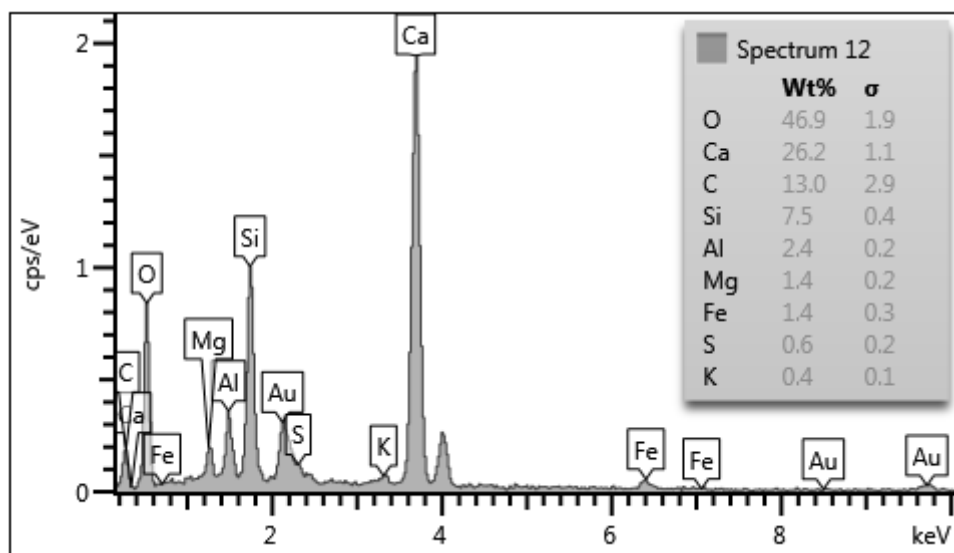


Figure 70 Spectrum analysis for YC50

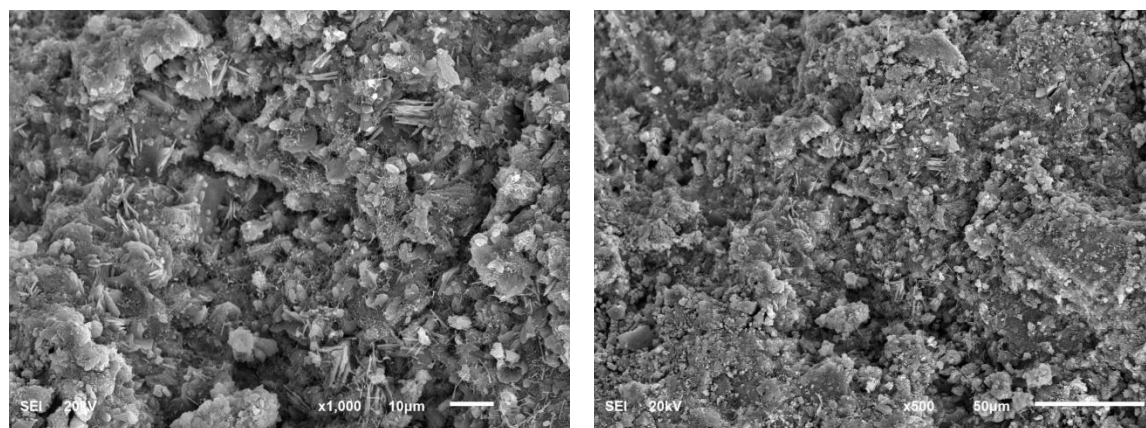


Figure 71 Micro image for YC70 with 10μm and 50μm magnification

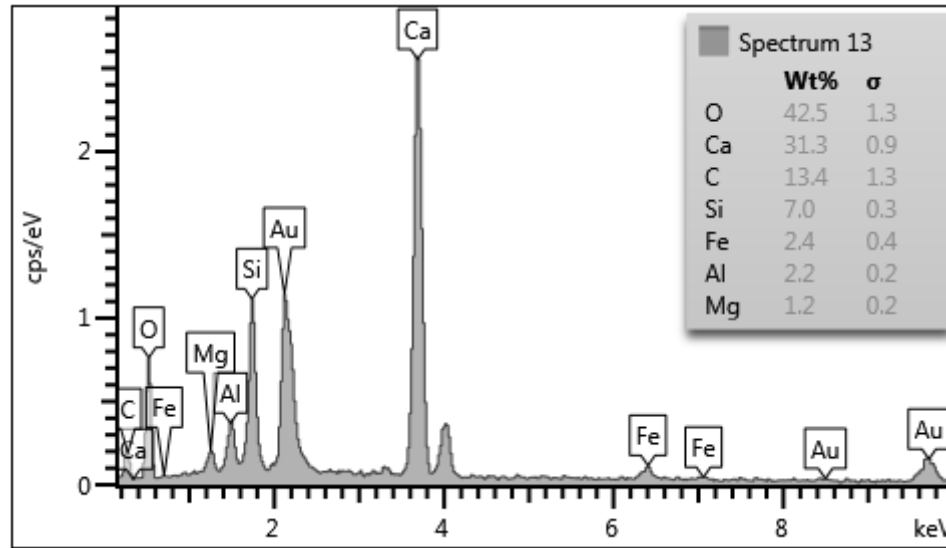


Figure 72 Spectrum analysis for YC70

Spectrum analysis show that the YC mainly contain of Ca, O, C, Si, Fe and Al. these results are matching the result obtained from XRF were the Si, Fe and Al are mainly coming from the clay and Ca were coming from the clinker. Increase in the clay the amount result in the increasing of Ca and Fe while other materials have small change or stay constant.

The results of SEM/EDS image for CM mixes are shown in figure 73 and 74:

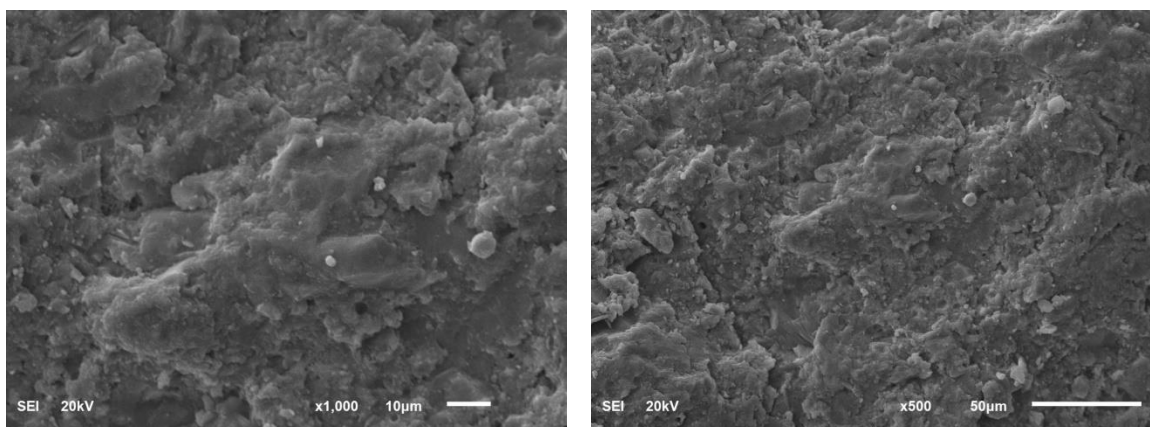


Figure 73 Micro image for CM with 10µm and 50µm magnification

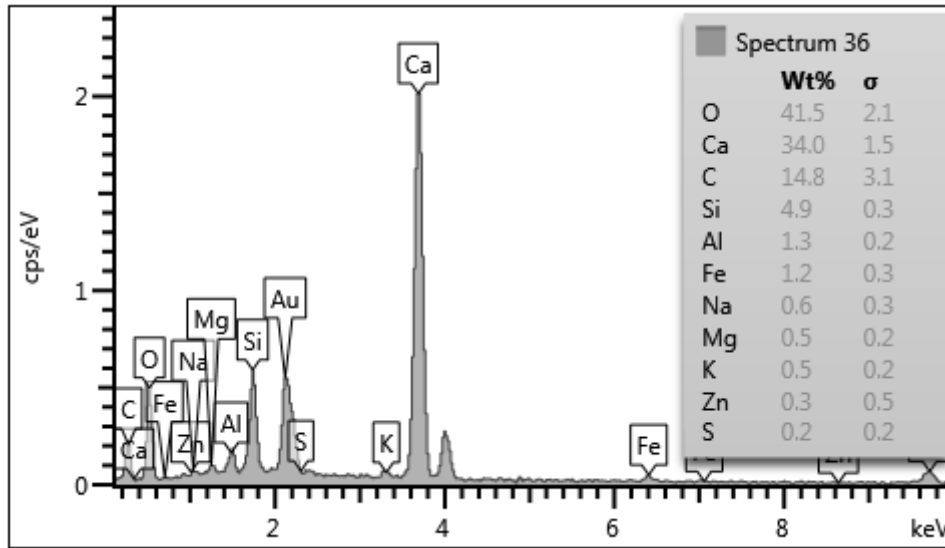


Figure 74 Spectrum analysis for CM

Spectrum analysis between LC3 mixes and CM show that LC3 for all clay types increase in Si and Al as it form silica (SiO_2) and alumina (Al_2O_3). Yuvaraj Dhandapani study show that inner CASH (calcium aluminum silicate hydrates) between CM and LC3 were uniform and similar defined composition while outer CASH region were various due to the pozzolanic reaction of LC3 also the inner and outer CASH have shown shift on LC3 composition compared with CM due to the reactive silica and alumina [40]. With finer materials (calcined clay and limestone) in LC3 mix it's reported to have smaller capillary pores as the reaction of metakaolin develop a denser microstructure that contribute in fill the capillary pores [14]. This reduction in capillary pores can result in enhancing the electrical resistivity and gas permeability [14,40].

4.6 Durability results

Durability tests LC3 concrete in two major aspects: concrete resistance to chloride penetration and concrete and paste resistance to sulphate and acid exposures.

4.6.1 Rapid chloride permeability test (RCPT)

Chloride resistance was tested with rapid chloride permeability test (RCPT). The test started after the samples were prepared. RCPT give a qualitative result according to the number of coulombs have passed throw the concrete ring sample the results of RCPT are shown in figure 75:

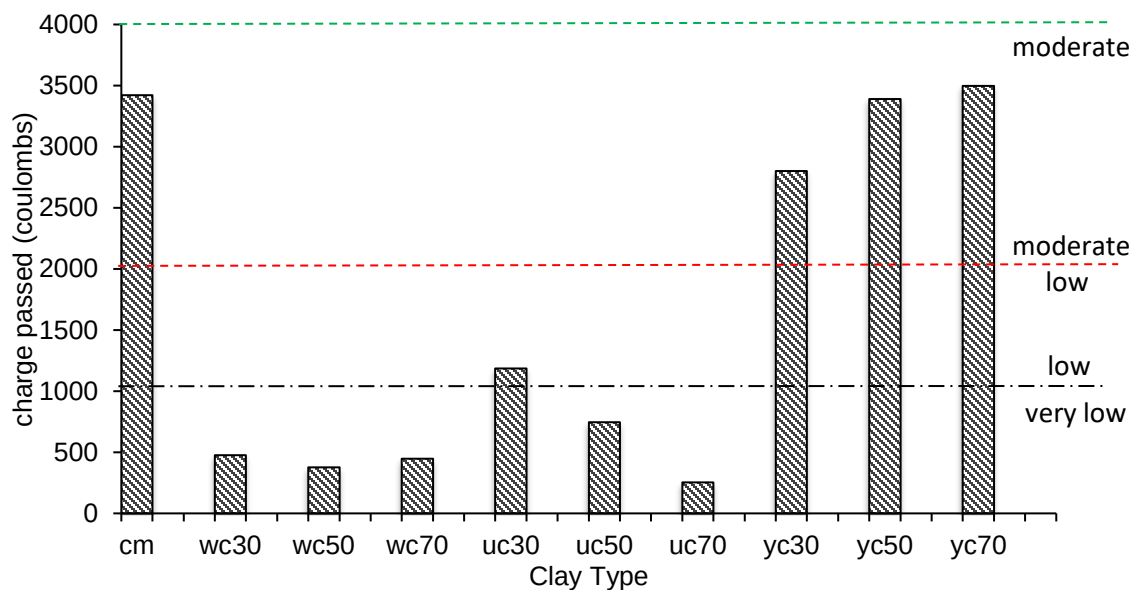


Figure 75 RCPT results for LC3 and CM.

The results of RCPT show that WC and UC have very low amount of charge passed were CM and YC having moderate RCPT reading. WC has similar result for all replacement. UC have a clear trend of decreasing the number of charged passing with increasing the clay content. This improvement in chloride resistance because of the refinement of the porosity

by the metakaolin and limestone that have higher resistance to ion transport and the presence of more reactive alumina resulting in high chloride resistance at early age [10,20,37]. YC clay have an opposite trend of UC which increase the number of charged passed with increase of clay content this may happened because YC clay have a higher iron content and the main oxides presenting in YC clay is calcium oxide (CaO) as shown in table 7 and 8 which is the main oxide in cement which make YC clay have similar charge pass as the CM mix.

4.6.2 Accelerated chloride migration test

Chloride penetration was tested also with accelerated chloride migration test. This test is measuring the penetration depth of the chloride throw the sample and measure the estimated rate of chloride penetration throw the sample. The results of accelerated chloride migration were shown in figure 76:

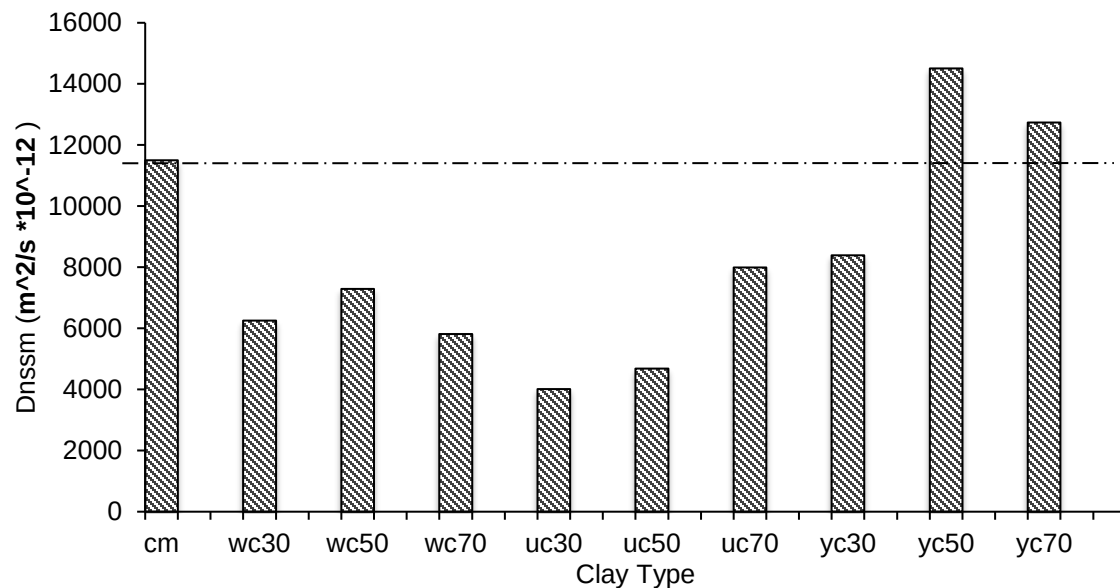


Figure 76 non-steady state chloride migration coefficient for LC3 and CM.

Accelerated chloride migration result show that UC and YC have higher rate of penetration with increase of clay while WC have result close to each other in case of penetration rate among the clay replacements. CM have higher penetration rate more than most of the clay types (except YC50/70). Yuvaraj Dhandapani show in his study the pozzolanic reaction of LC3 were improving chloride resistance for LC3 also there is strong correlation between RCPT and the non-steady state chloride migration coefficient as both test show and improvement in chloride resistance with LC3 mix compared with CM [10].

4.6.3 Sulphate exposure

Sulphate exposure was tested for 2 and 4 months, the sulphate solution were 5% concentration (2.5% sodium sulphate and 2.5% magnesium sulphate). The test has studied the effect of the sulphate on weight loss, appearance and compressive strength. The test was performed on concrete cube (50*50*50) mm and paste cubes (25*25*25) mm. The change in concrete samples appearance is shown in figure 77 and 78 for 2 and 4 months respectively:

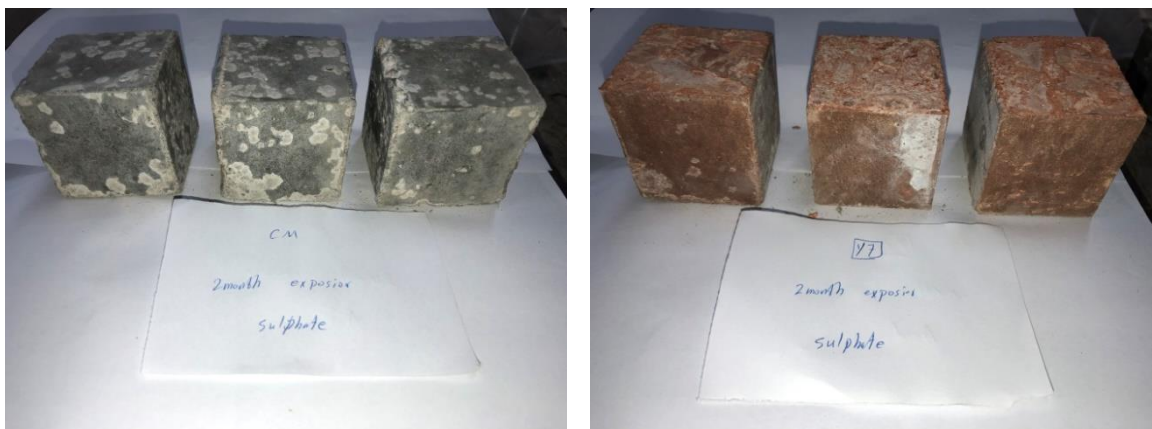


Figure 77 Change in appearance on concrete cube after 2-month sulphate exposure

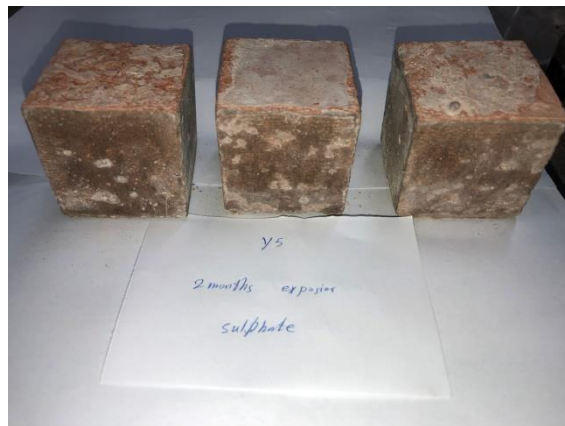
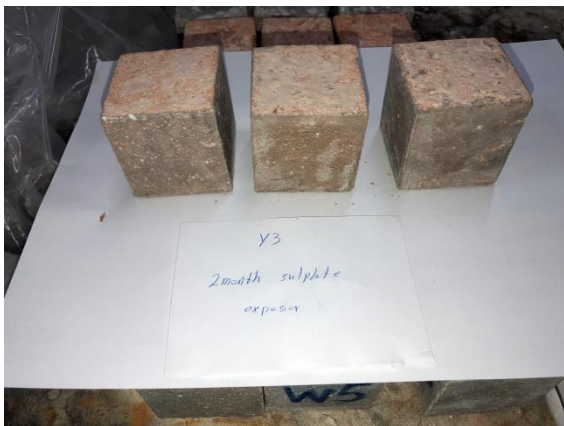
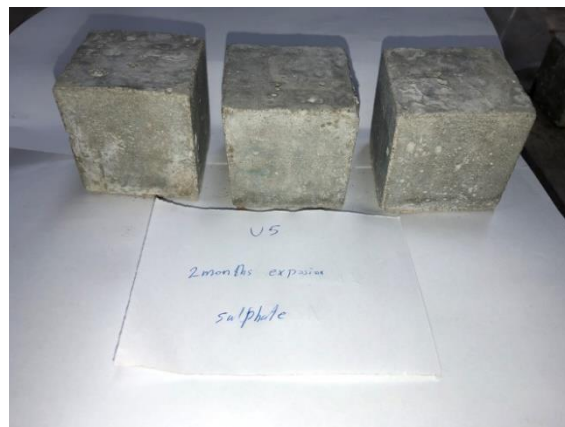
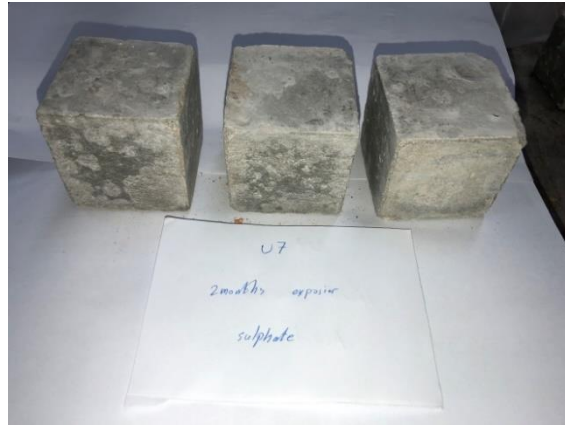
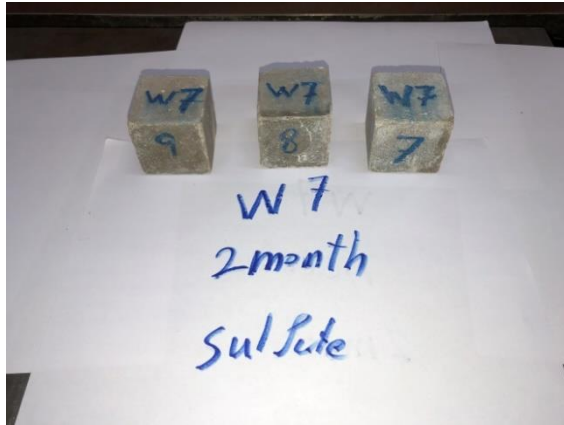


Figure 78 Change in appearance on concrete cube after 2-month sulphate exposure

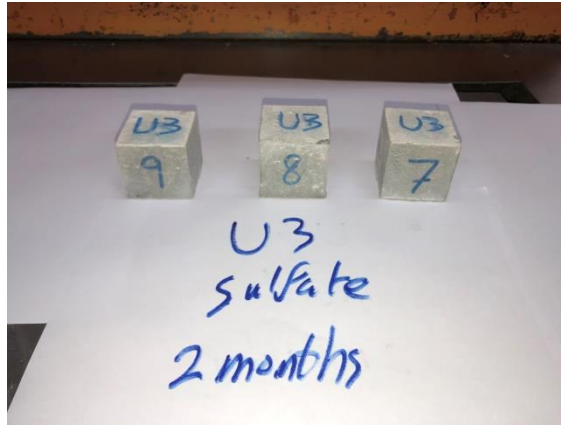


Figure 79 Change in appearance on concrete cube after 2-month sulphate exposure

From these photos taken for the concrete samples, the damage happen is small only some edges have become less sharp that before and only the color of the outer surface has some stains caused by the sulphate exposure after 2 months.



Figure 80 Change in appearance on concrete cube after 4-month sulphate exposure

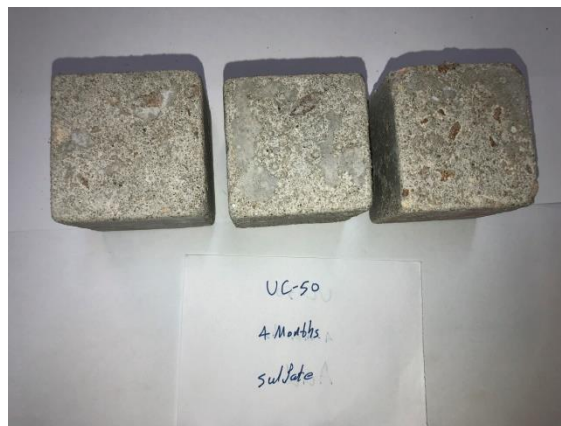
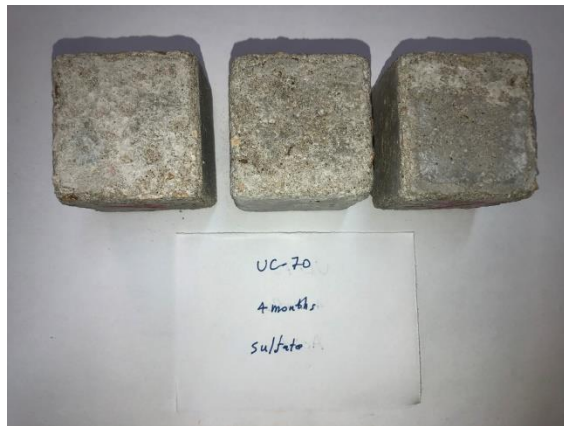


Figure 81 Change in appearance on concrete cube after 4-month sulphate exposure



Figure 82 Change in appearance on concrete cube after 4-month sulphate exposure

From these photos taken for the concrete samples after 4 months exposure the damage happen is higher than 2 months with increase of losing the edges and more change on the surface color of the samples caused by the sulfate exposure.

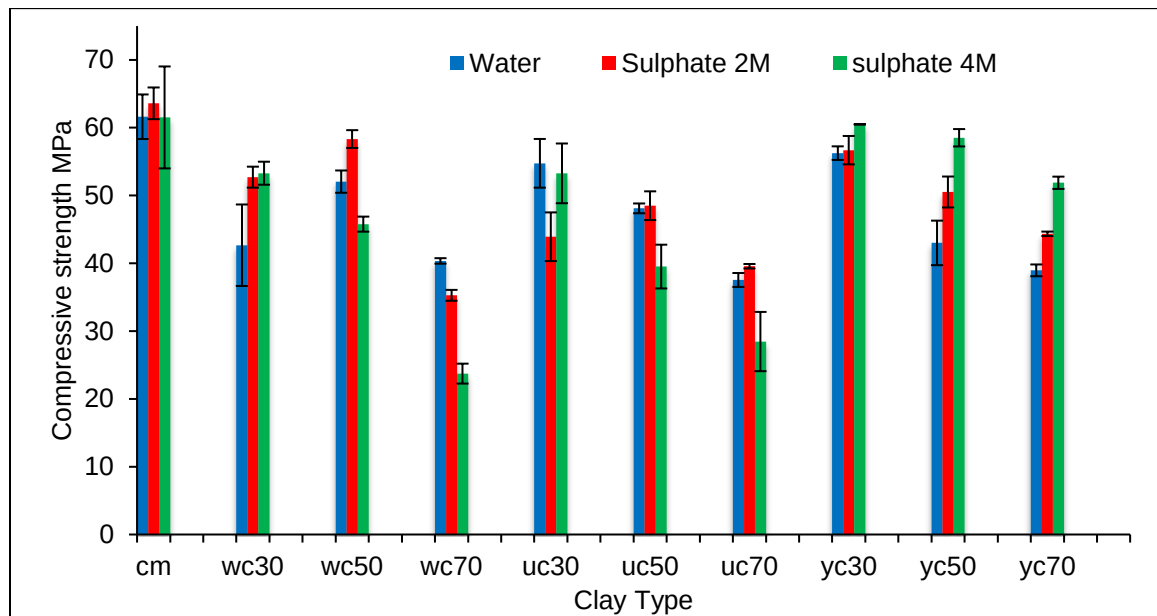


Figure 83 compressive strength of sulphate exposure for concrete

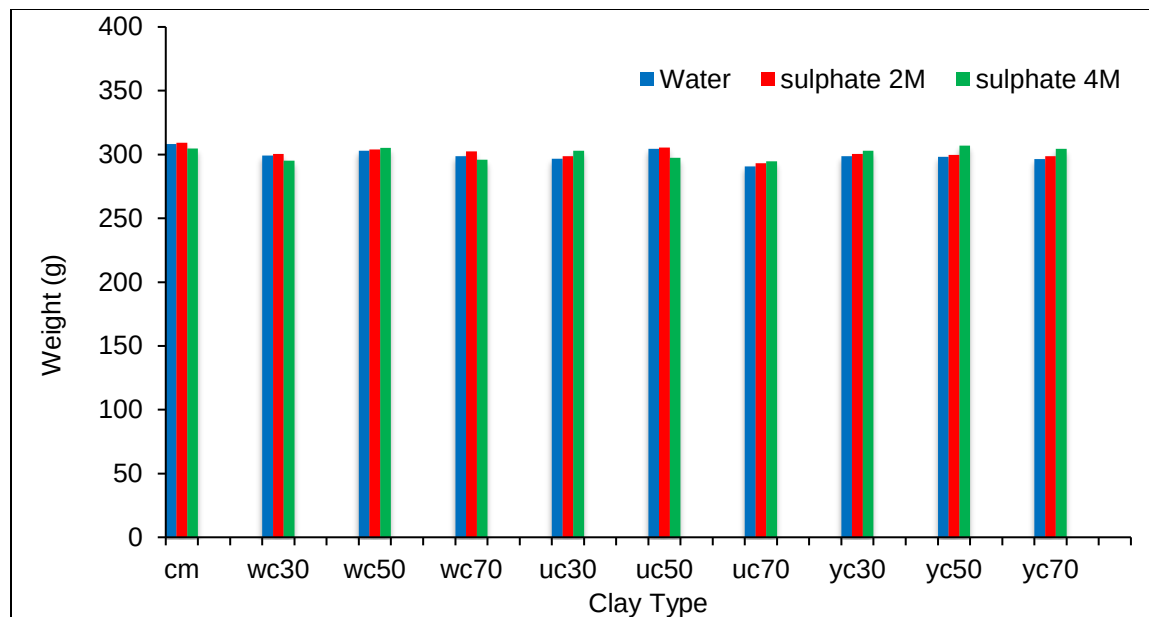


Figure 84 weight loss of sulphate exposure for concrete

The first graph shows a comparison in concrete compressive strength between samples that have exposed to sulphate for 2 and 4 months with samples that have kept under water. The sulphate exposure has a little enhancement in the compressive strength compared to control samples or having the same strength. Generally, the change in compressive strength is low between the exposed samples and control samples. Also, the weight of the sample is almost the same the small additional weight in the sample is caused by absorbing some of the sulphate into the concrete.

The same behavior can be noticed on the paste cubes in figure 80 for 2 months and figure 81 for 4 months. The change in compressive strength and weight are shown in figure 82 and 83 respectively:

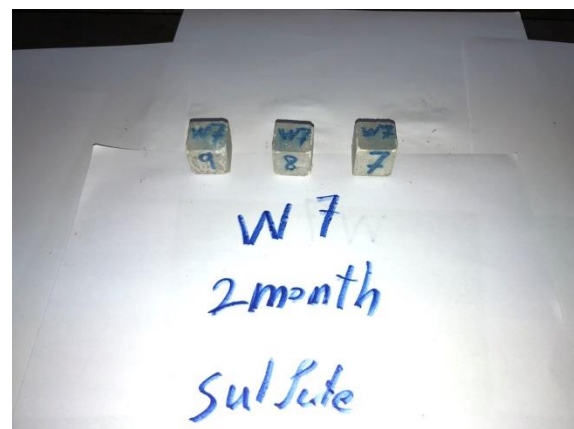
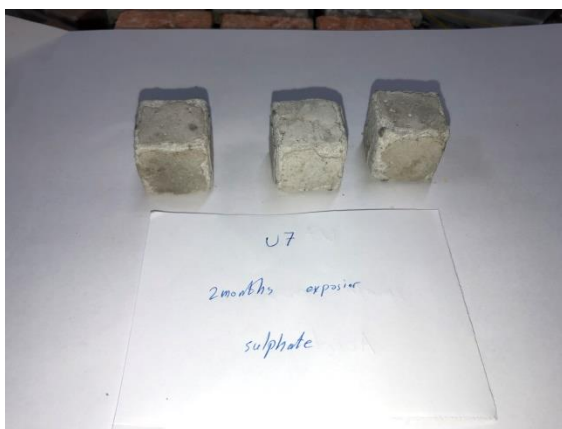
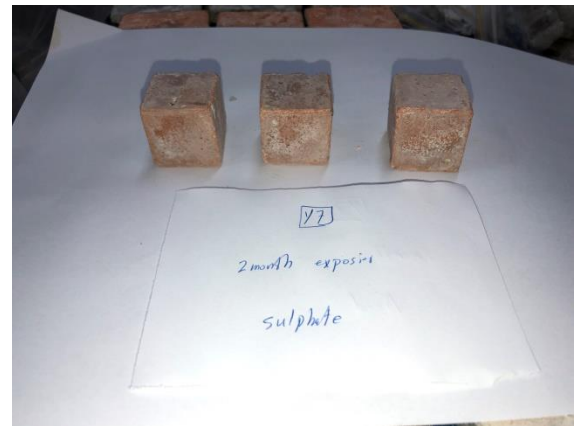


Figure 85 Change in appearance on paste cube after 2-month sulphate exposure.

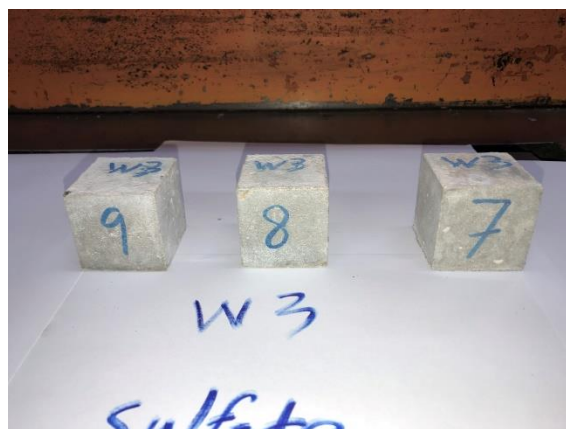
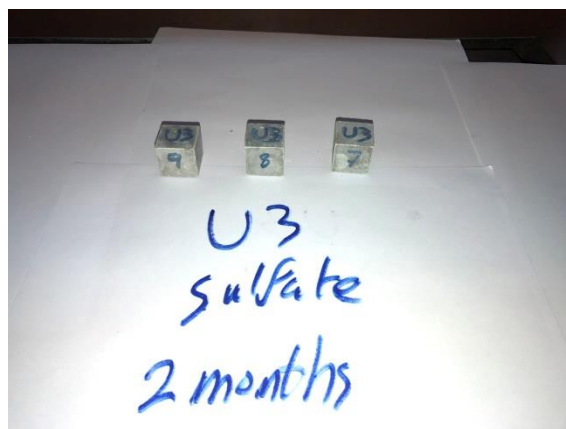


Figure 86 Change in appearance on paste cube after 2-month sulphate exposure.



Figure 87 Change in appearance on paste cube after 4-month sulphate exposure.



Figure 88 Change in appearance on paste cube after 4-month sulphate exposure.

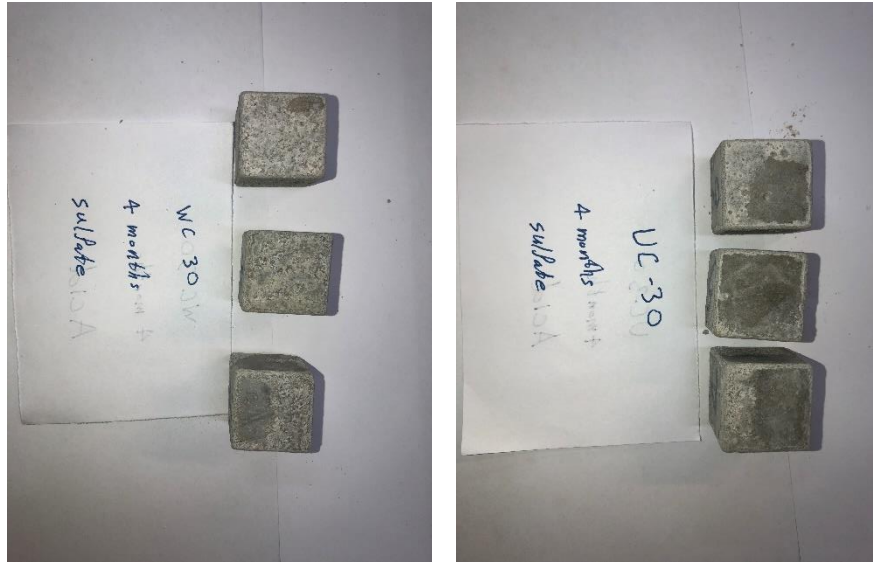


Figure 89 Change in appearance on paste cube after 4-month sulphate exposure.

From these photos taken for the paste samples the damage happen is small only some edges have become less sharp that before and only the color of the outer surface has some stains caused by the sulphate exposure.

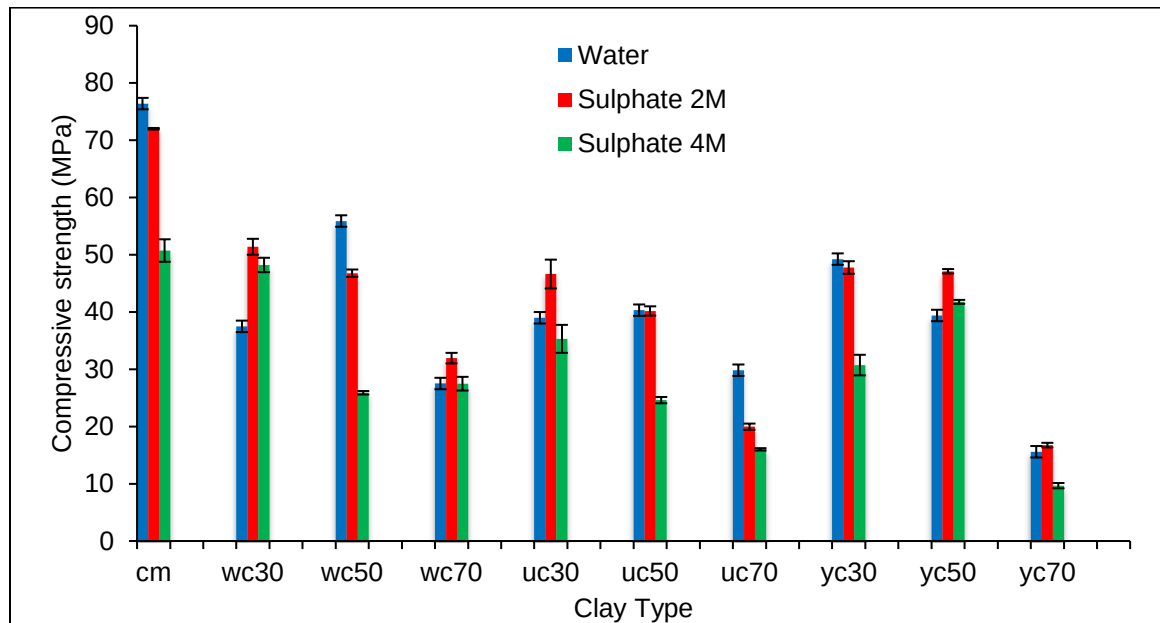


Figure 90 compressive strength for sulphate exposure for paste samples.

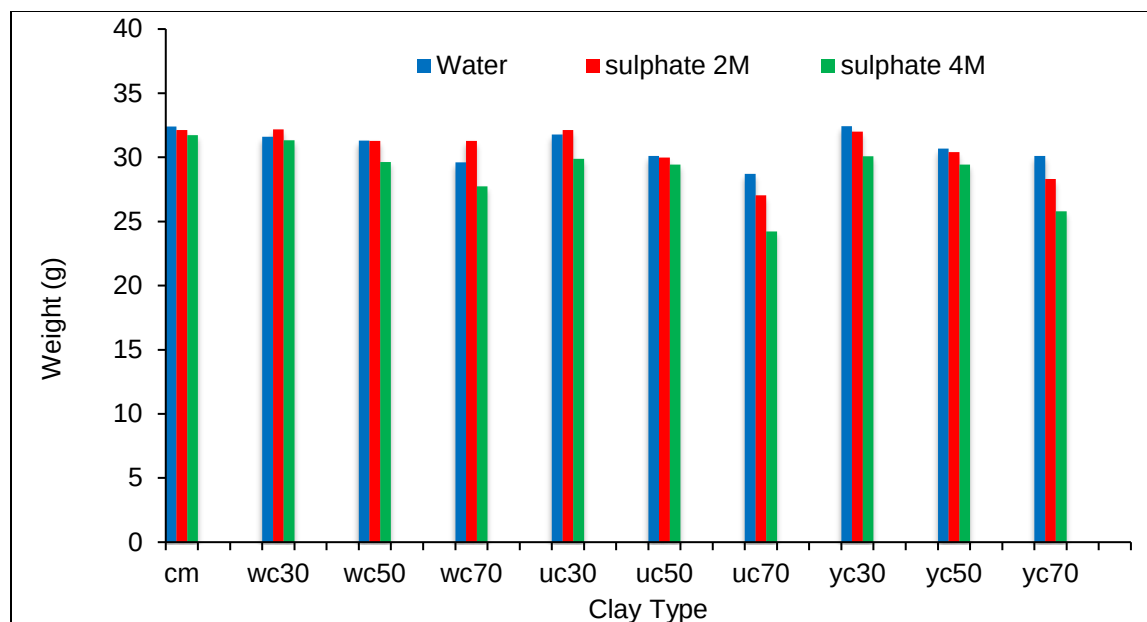


Figure 91 weight loss for sulphate exposure for paste samples.

The first graph shows a comparison in paste compressive strength between samples that have exposed to sulphate for 2 and 4 months with samples that have kept under water. The sulphate exposure samples have a little enhancement in the compressive strength compared to control samples or having the same strength with 2 month exposure while with 4 months exposure the strength is start to decrease. Generally, the change in compressive strength is low between the exposed samples and control samples. Also, the weight of the sample is almost the same or have small reduction.

The pozzolanic reaction in LC3 by the metakaolin and limestone have shown good resistance to sulfate attack as with 5% solution concentration with duration of 2 months there was no effect on the sample [17,39]. Another study made by Al-Amoudi studied the effect of the sulfate attack on plain and blended cement shows that the main factor of the increase in sulfate resistance was the reduction of portlandite in the blended cements and the densification of these cements [43]. In LC3 cement the portlandite is reduced as have

been shown in XRD results in for all clay types and the mixture have more density than CM.

4.6.4 Acid exposure

Acid exposure was tested for 2 and 4 months. The Acid solution had a concentration of 3% sulfuric acid. The test has studied the effect of the acid on weight loss, appearance and compressive strength. The test was performed on concrete cube (50*50*50) mm and paste cubes (25*25*25) mm. after the 2 and 4 months, the change in appearance in concrete cubes is clear as shown in figure 84 and 85 respectively. Compressive strength and weight loss are shown in figure 86 and 87:

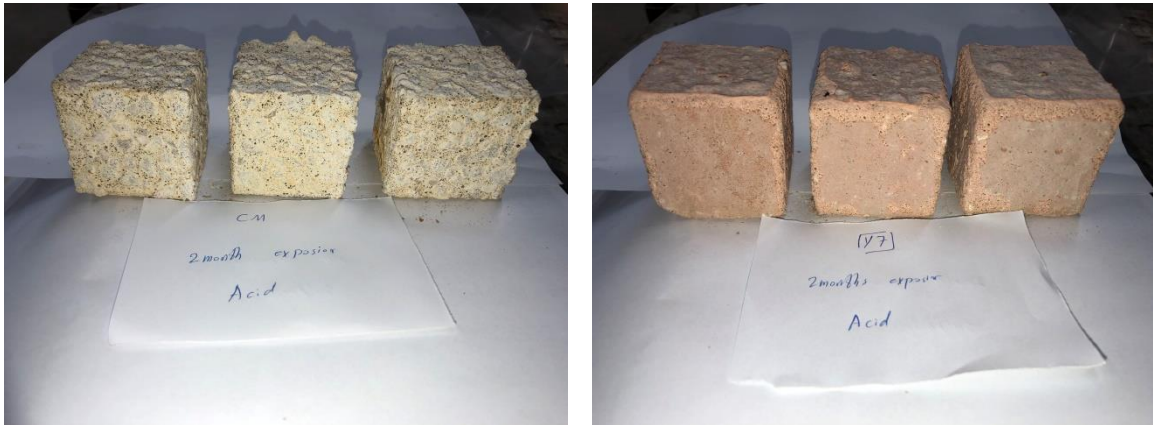


Figure 92 Change in appearance on concrete cube after 2-month acid exposure.

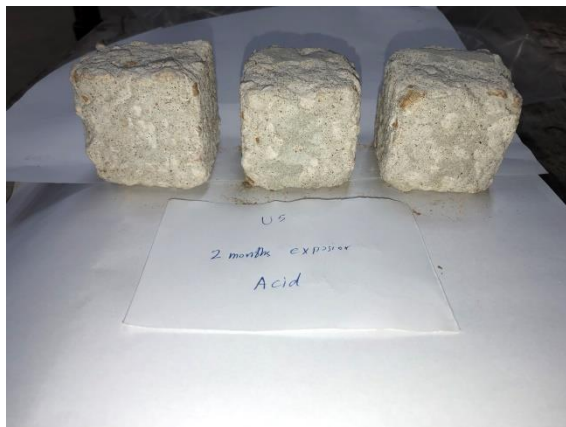
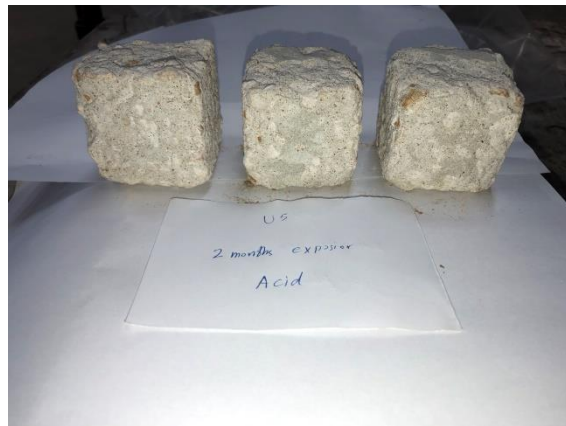
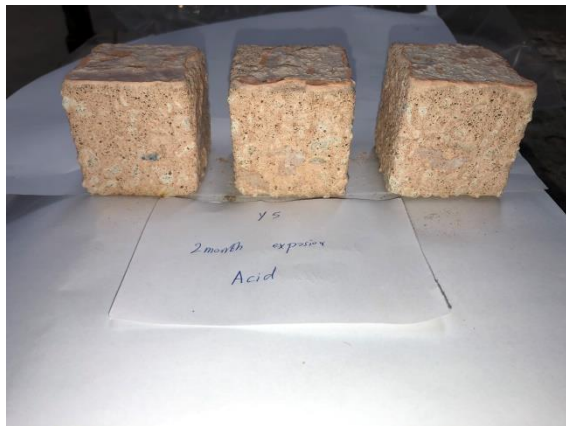
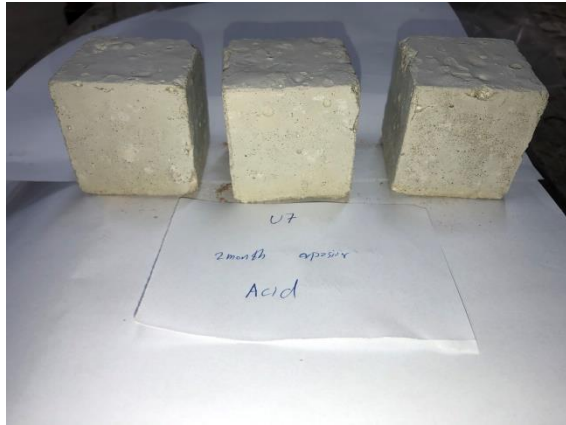


Figure 93 Change in appearance on concrete cube after 2-month acid exposure.

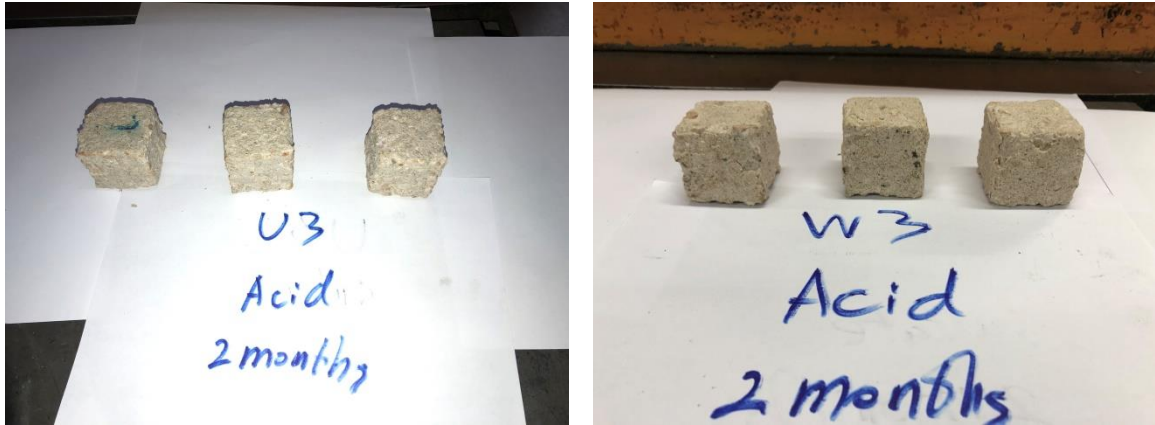


Figure 94 Change in appearance on concrete cube after 2-month acid exposure.

From these photos taken for the concrete samples the damage happen clearly on the acid exposure samples. The outer layer of the cube sample has completely fall on CM and in LC3 with 30% and 50% replacements. The 70% show a good resistance to acid exposure the outer layer have some damage but still not falling only the edges have become less sharp and there are change on the surface color.

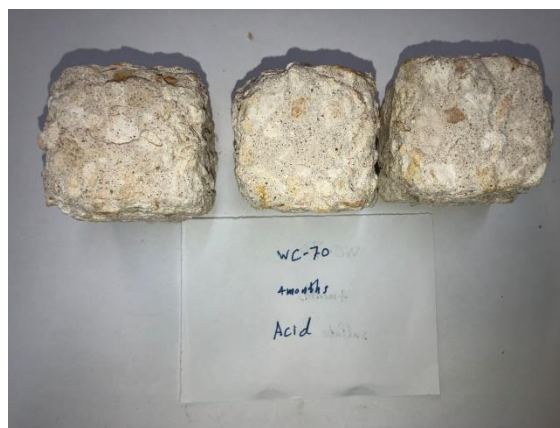
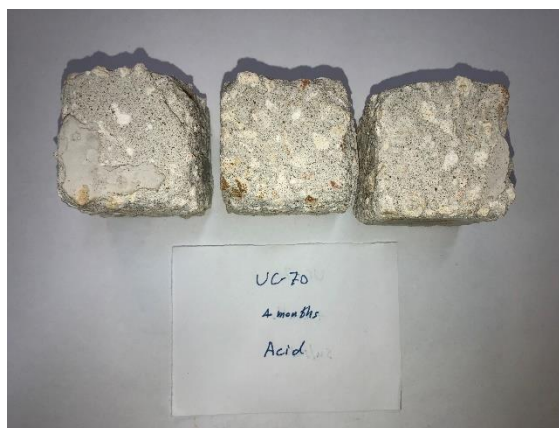
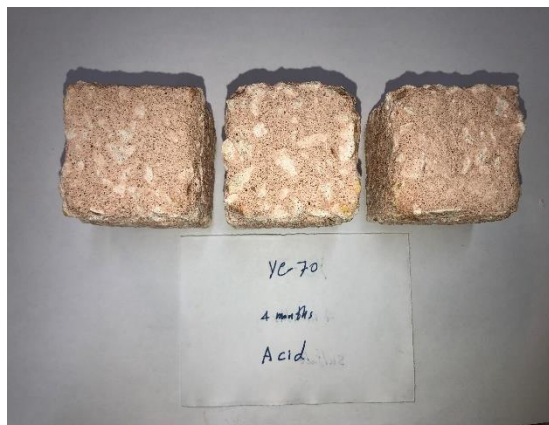
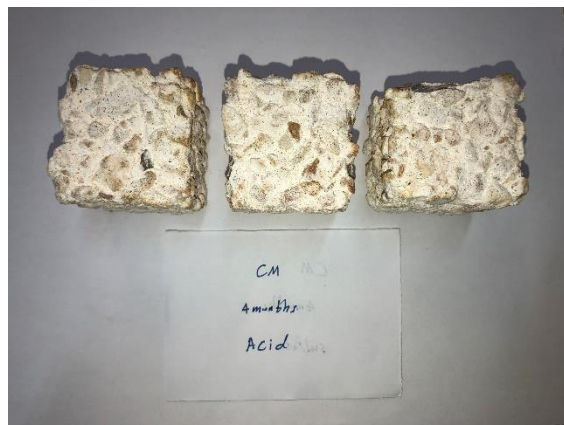


Figure 95 Change in appearance on concrete cube after 4-month acid exposure.



Figure 96 Change in appearance on concrete cube after 4-month acid exposure.

From these photos taken for the concrete samples the damage happen clearly on the acid exposure samples. The outer layer of the cube sample has completely fall on CM and LC3 with 30%, 50% and 70% replacements. The 70% with YC clay have shown a better resistance to acid exposure compared with other mixes with 4 months duration.

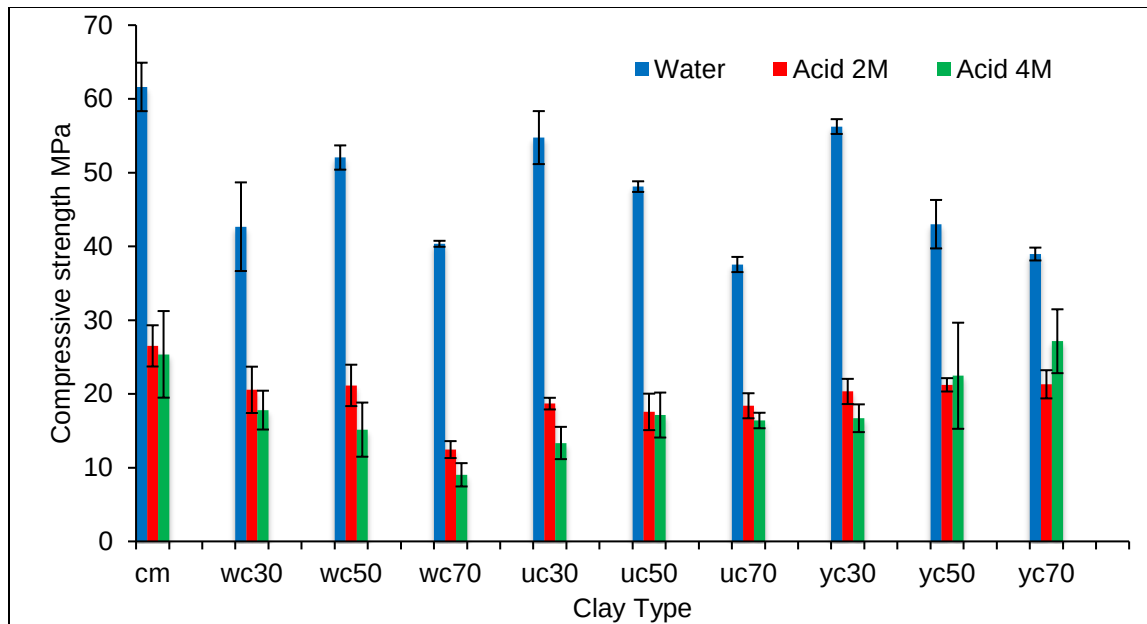


Figure 97 Compressive strength of acid concrete exposed sample compared with water cured samples.

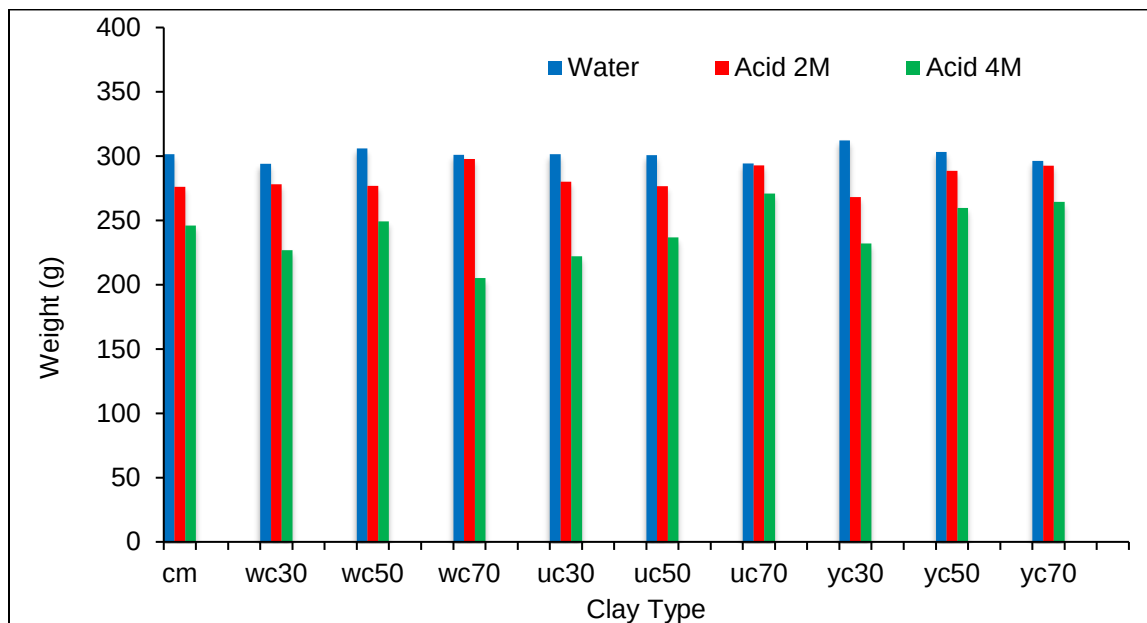


Figure 98 weight loss of acid concrete exposed sample compared with water cured samples.

The first graph shows a comparison in concrete compressive strength between samples that have exposed to acid for 2 and 4 months with samples that have kept under water. The effect of the acid exposure was a high drop in strength by half the strength compared with control samples in CM and LC3 with all replacement and the reduction is increasing with

4 months exposure. This shows that the clay in LC3 have no improvement on the resistance against acid exposure in respect with compressive strength. The change in weight as shown graph 87 show there is a little drop on the weight by 8% in CM and LC3 with 30% and 50% replacement caused by the drop of the outer layer while the 70% replacement have a very low drop in weight (1-2) % caused by the removing of the sharp edges in 2 months. While in 4 months duration the reduction in weight is increased to 15% to 18% for all the mixes of LC3 and CM caused by removing the outer layer of binder and exposing the outer coarse aggregate.

The same behavior can be notice on the paste cubes in figure 88 and 89 for paste sample in 2 and 4 months. The change in compressive strength and weight are shown in figure 90 and 91:

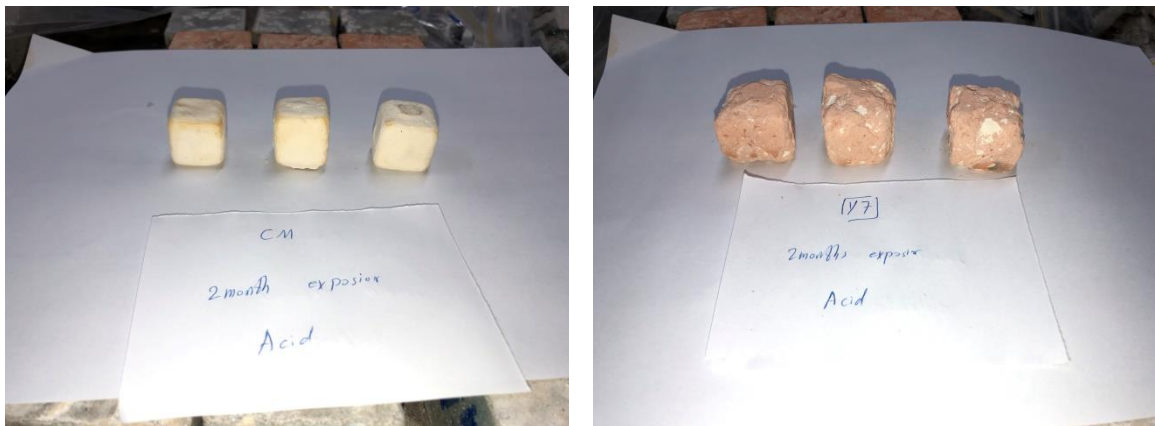


Figure 99 Change in appearance on paste cube after 2-month acid exposure.

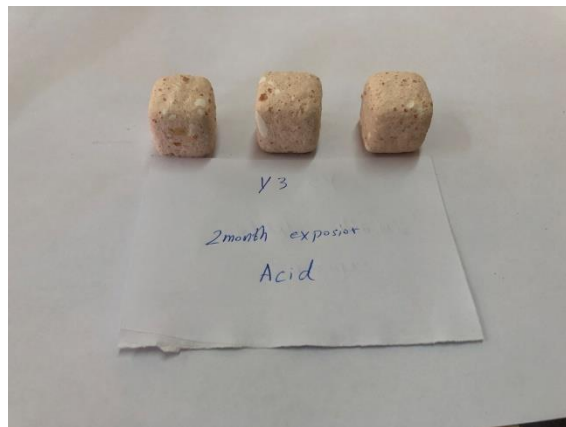
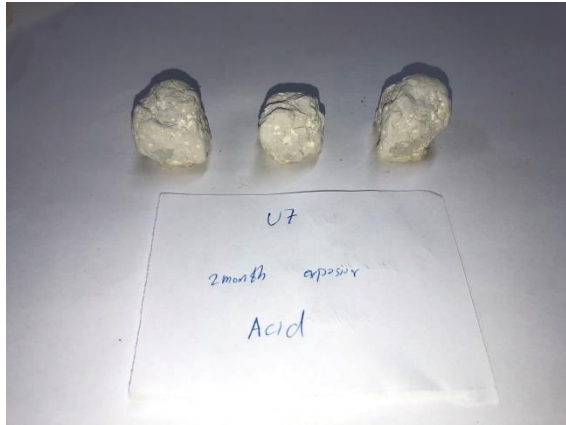


Figure 100 Change in appearance on paste cube after 2-month acid exposure.

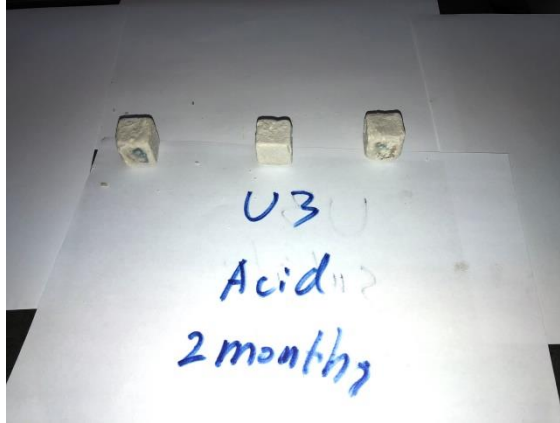


Figure 101 Change in appearance on paste cube after 2-month acid exposure.

From these photos taken for the paste samples, the damage on the samples is clearly on after acid exposure. The outer layer of the cube sample has completely fall in all samples and the damage was uniformly which cause the new surface to be smooth. The 70% of UC and YC have irregular damage which cause to irregular shape after 2 months exposure. A change in color was clear in all samples and all samples have lost its sharp edges.

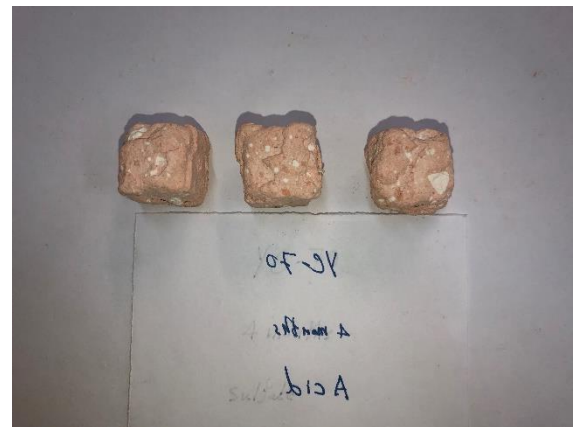


Figure 102 Change in appearance on paste cube after 4-month acid exposure.



Figure 103 Change in appearance on paste cube after 4-month acid exposure.



Figure 104 Change in appearance on paste cube after 4-month acid exposure.

From these photos taken for the paste samples, the damage clearly on the acid exposure. The outer layer of the cube sample has completely fall in all samples and the damage happened completely to other samples. The new surface was irregular after 4 months exposure. The 70% YC was the best mix to resist the acid exposure as the shape of the sample still uniform with some edges.

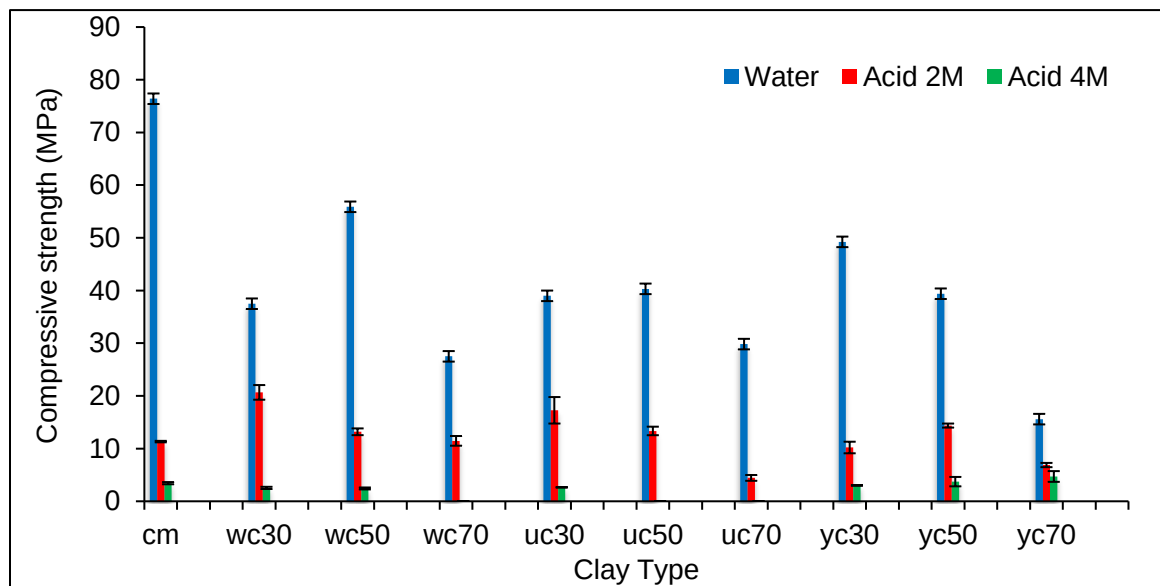


Figure 105 Compressive strength of acid paste exposed sample compared with water cured samples.

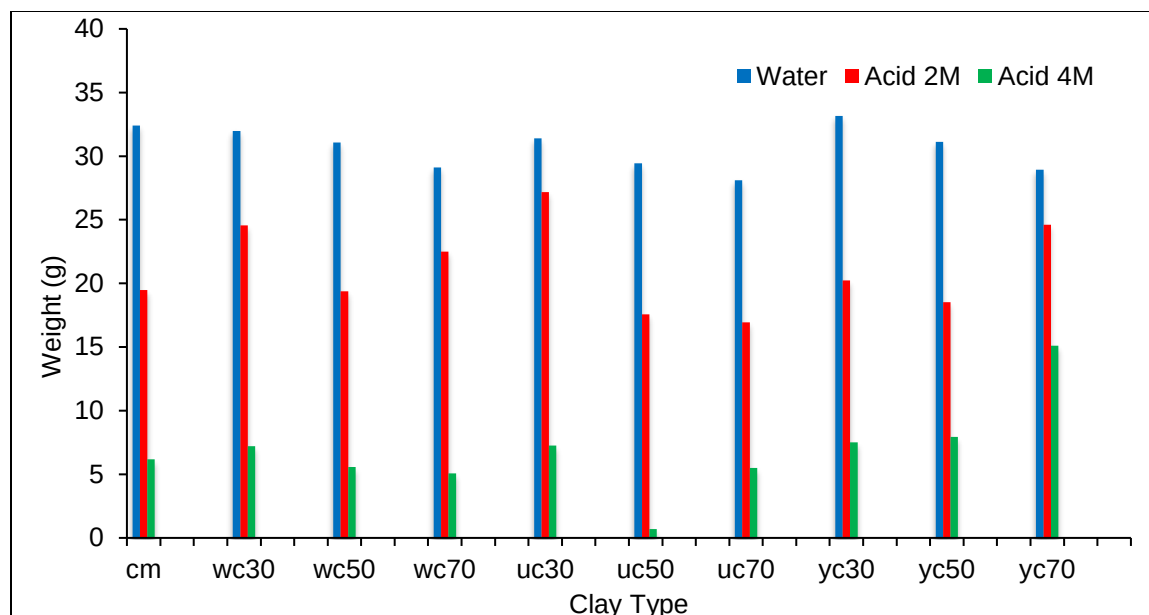


Figure 106 Weight difference before and after the acid paste exposure.

The first graph shows a comparison in paste compressive strength between samples that have exposed to acid for 2 and 4 months with samples that have kept under water. The samples after the acid exposure have a high drop in strength by more than half compared with control samples in CM and LC3 with all replacement. This shows that the clay in LC3 have no improvement on the resistance against acid exposure in respect with compressive strength. In 4 months, exposure the compressive strength drops to lower than 5 MPa with reduction of more than 80%. The change in weight as shown graph 91 show there is a drop on the weight by (5- 25) % for 2 months samples cause by the drop of the outer layer in all mixes while in 4 months samples the drop in weight increase to 70% compared with samples cured under water.

Resistance to acid exposure mainly depends on the raw materials that included in the mix. It's been reported that mixes with rich amount of calcium Ca have negative effect on the resistance to sulfuric acid as they can react and form CaSO_4 (gypsum) the reaction between the sulfuric acid and calcium from CSH (Calcium silicate hydrate) to form gypsum which

decrease the mechanical strength of the concrete after the exposure [44,45]. While low calcium mix have performed better in case of resistance to acid exposure [46]. LC3 mix has fewer amounts of calcium compared with CM depending on the amount of metakaolin substitution. XRF results show that WC and UC have small to (neglected) amount of calcium which can relate to their higher performance to resist acid attack especially with 70% replacement while YC which have high calcium have shown no difference compared with CM. WC and UC have also good amount of aluminum which forming CASH resulting in denser structure as fewer pores form that slow the diffusion of (H^+) resulting in more resistance for acid [47].

CONCLUSION

This study aimed to study the kaolinite clay that are available locally or in the market and its ability to generate LC3 concrete that have similar properties to normal concrete in order to see if it can be used as structural concrete. This thesis studied 3 different types of clay local white clay WC, Ukrainian clay UC and local yellow clay. These clays have prepared by crushing calcination to be usable in concrete mix and compared with a control mix contain only normal concrete. 3 level of replacement were studied 30%, 50% and 70% for each type of clay and studied in characterization of raw clay, fresh properties of LC3, mechanical properties, characterization of hydrated LC3 and durability aspect.

Characterizations of raw clays showed that the clay tested had a decent amount of kaolinite in order to make LC3 concrete. The availability of kaolinite was tested by XRD and TGA analysis.

Fresh properties mainly focused on the water demand and flowability of LC3 paste and concrete. The effect of clay and lime stone were clear of increasing the water demand with decreasing the flowability of LC3 paste. This lead to increase of the time needed for the mix to set and hardened. In case of concrete, a dosage of superplasticizer was needed to make a good flowable concrete.

LC3 show acceptable strength to make structural concrete with 30 MPa strength developed over time period of 28 days for 30% and 50% replacement while 70% replacement reached 30 MPa at 90 days. Similar result was found on LC3 paste and mortar of delaying in gain of strength when the amount of clay increased. Modulus of elasticity has improved in LC3

to 38 GPa in comparison with 30 GPa in CM. LC3 have shown less shrinkage compared with CM in duration of 30 days.

Micro-structure result shows the initial component of each type of clay, limestone and gypsum and the resulting component after the hydration was depending on the replacement rate. Generally the main component of hydrated materials is ettringite, portlandite, hydrocalumite and calcium carbonate. The result of both XRD and SEM/EDS has shown the same result of the formation of these materials.

RCPT on LC3 have shown great result compared with CM as very low penetration were achieved in WC and UC clay. Were YC having no improvement in chloride resistance as it have similar result with CM. Accelerated chloride migration penetration show that LC3 have some improvement in case of lower penetration rate than CM and have less penetration depth.

Sulphate exposure of 5% concentration has applied on LC3 in duration of 2 months. As shown the sulphate had a very small damage on the LC3 in case of changing the surface color and reducing the sharpness of the samples edges. But, some increase in compressive strength after the exposure were noticed without reduction in weight for each sample.

Acid exposure of 3% has shown a great amount of damage on LC3 in duration of 2 months. In LC3 with 30% and 50% replacement the surface layer of the samples were completely removed and lost all the sharp edges on the sample while 70% replacement showed a good resistance compared with 30% and 50% were the outer surface layer have little damage only change in color and removing of sharp edges happened. A 50% reduction on compressive strength can be noticed after the exposure in all replacement levels. reduction

of weight happens in 30% and 50% replacement with 8% reduction of weight, while 70% have a reduction with (1-2) % of weight.

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